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Study of materials, technique and conservation treatment of *Sinfonia Heroica*
by Dordio Gomes

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INTRODUCTION

The painting *Sinfonia Heroica/Beethoven* (1948) by the Portuguese painter Simão César Dordio Gomes belonging to Culturgest presented several conservation issues that, allied to the institutions needs, were well suited for a painting conservation internship.

On one hand, the painting presented several current conservation problems: tears, lacunas, and support distortions etc. which, generally, to every similar case; conservators tend to apply the same known methods to them. On the other hand, it also presented conservation issues that required a more detailed material study of its genesis and appearance: for example the interlaminar cleavage between paint layers was resulting in detachments (which was initially observed on the upper side of the painting where there was a thicker density of paint but then, after close observation was visible in other areas as well). The painting was severely distorted (out of plane distortions). To reduce distortions a well controlled moisture treatment/flattening regime was required, and due to the paintings size, had to be carefully designed.

After observing other paintings by the same artist, in Museu Nacional Soares dos Reis (MNSR) and in the painter's son's house, it was established that the problem of interlaminar cleavage and detachment of the top layers was not isolated to *Sinfonia Heroica/Beethoven*. The main question was if this issue was due to the painter's technique or, due, to his material's composition or any other physical or chemical change (metallic (zinc) soap formation, or binder components' migration to the interlaminar areas). Therefore, it was absolutely necessary to perform a study on the painter's methods, techniques and materials that would illuminate the root causes of the technical problems.

For the study of methods and techniques, it was essential to interrelate information provided by the Artist's son, Architect Dordio Gomes, with observations of his other works and the exams and analyses of the painting, including his paint tubes. The analyses to characterize his materials and techniques were primarily non-destructive: Visible, transmitted, raking, IR and UV photography as well as μ -XRF *in situ* analyses; Micro-samples for cross-sections were examined with the optical microscope (OM) observation, μ -XRF, EDX-SEM and μ -Raman analyses. Other micro-sampling was run as a one day's workshop at the DCR laboratory (with the help of the *Crossing Borders* researchers) and focussed on characterization of the pigments, varnish and binder through μ -Raman and μ -FTIR.

The biggest conservation challenge in terms of treatment was the painting's manipulation, for it's such a heavy and large painting (1,78x1,47 cm without frame). In this way, what would be a normal daily routine for a small painting with severe canvas support distortions, for *Sinfonia Heroica* became a huge project where every step of the process had to be carefully studied and where there was no room for mistakes. This part of the process was very slowly and thoroughly studied using imaginative ideas and many different starting approaches that related to how the flattening treatment would be accomplished. At the end, it was established that the best way was to have in all flattening steps, the painting face up because of the interlaminar cleavage issue and detachment problems. To achieve flattening a humidifying tent was designed and prepared where it would be possible to achieve the desired relative humidity (RH) in a controlled manner. To accomplish the flattening treatment totally flat surfaces would be required, that would support the total area of the painting uniformly. Within the studio it was necessary to have large, flat surfaces to work on as well as numerous human resources for assistance.

As stated by James France in the foreword of the book *Big Pictures*: "Many conservators will, at some time of their career, face the challenge of tackling a large-scale project that tests their previous experience" [1].

The Internship was held at the Conservation Department at the New University, Faculty of Sciences and Technology, and the conservation treatment was carried out in the painting conservation laboratory.

CHAPTER I: INTRODUCTION AND DESCRIPTION OF THE PAINTING

1.1 DESCRIPTION OF THE PAINTING

Category: Painting on Canvas

Artist: Gomes, Simão César Dordio

Title: *Sinfonia Heroica* (title on wooden plate attached to the frame)

Date: 1948 (dated on the bottom left, "48"), 20th Century.

Dimensions: 178 x 147 cm (without frame); 191x160x6 cm (with Frame)

Signature: Dordio Gomes (Signed and dated at bottom left corner, "Dordio 48", Fig.1, page 4)

Owner: Culturgest/ Caixa Geral de Depósitos Collection (CGD)

Inventory Number: 34657

1.2 BRIEF DESCRIPTION OF THE IMAGE :

The painting has a vertical rectangular format. Represented in the foreground, is a full-length male figure rising from a ravine, figure's right arm held high. The background appears to illustrate an emotionally troubled and complex scene. The title of the work, *Sinfonia Heróica* (Heroic Symphony) indicates that the figure which occupies about 50% of the painted area is a representation of Ludwig Van Beethoven (author of "Eroica" Symphony). The male figure is dressed with a blue suit and over top, wears a long brown coat that appears to flow to the back because of the wind. Around his neck, he wears a red scarf. The scenery in the background represents a distorted reality: at the upper right side there is an allusion to Napoleon's French troops, underneath is the figure of Napoleon riding a white horse. At the bottom right, is a female figure with a long white dress and raised arms, which seems to soar above the background colour. The loose brushwork and rapid execution prevent the recognition of details. The painting displays strong dark colours with violent contrasts, where dark blues and greens as well as red / brown colours are dominant.

With the naked eye, the pictorial layers present heterogeneous thicknesses: most of the painting shows fluid brushstrokes, applied in thin layers although, in some areas like Beethoven's face and the area with the troops, there's high density and concentration of paint built up in impasto.

1.3 RECENT PROVENANCE :

According to the Culturgest Matriz file (document with work identification), the painting was incorporated In the CGD collection on 10, November, 1994. At that time, it was placed in the CGD art storage situated in Anjos (Reserva dos Anjos, 39 V). Between December 2000 and January 2001, the storage area suffered a water flood¹, meaning that during this period, the painting was subjected to very high relative humidity.

On 5th of June 2008, the painting was moved to Culturgest's new storage area (Reservas do Lumiar, room 2, painting storage panels). This storage offers very good and stable environmental conditions appropriated for paintings: controlled relative humidity (RH) and temperature (T°) recorded by computer, with a fire control system and closed sliding metal panels for the painting racks.

¹ Information provided by Isabel Corte-Real, CGD collection curator

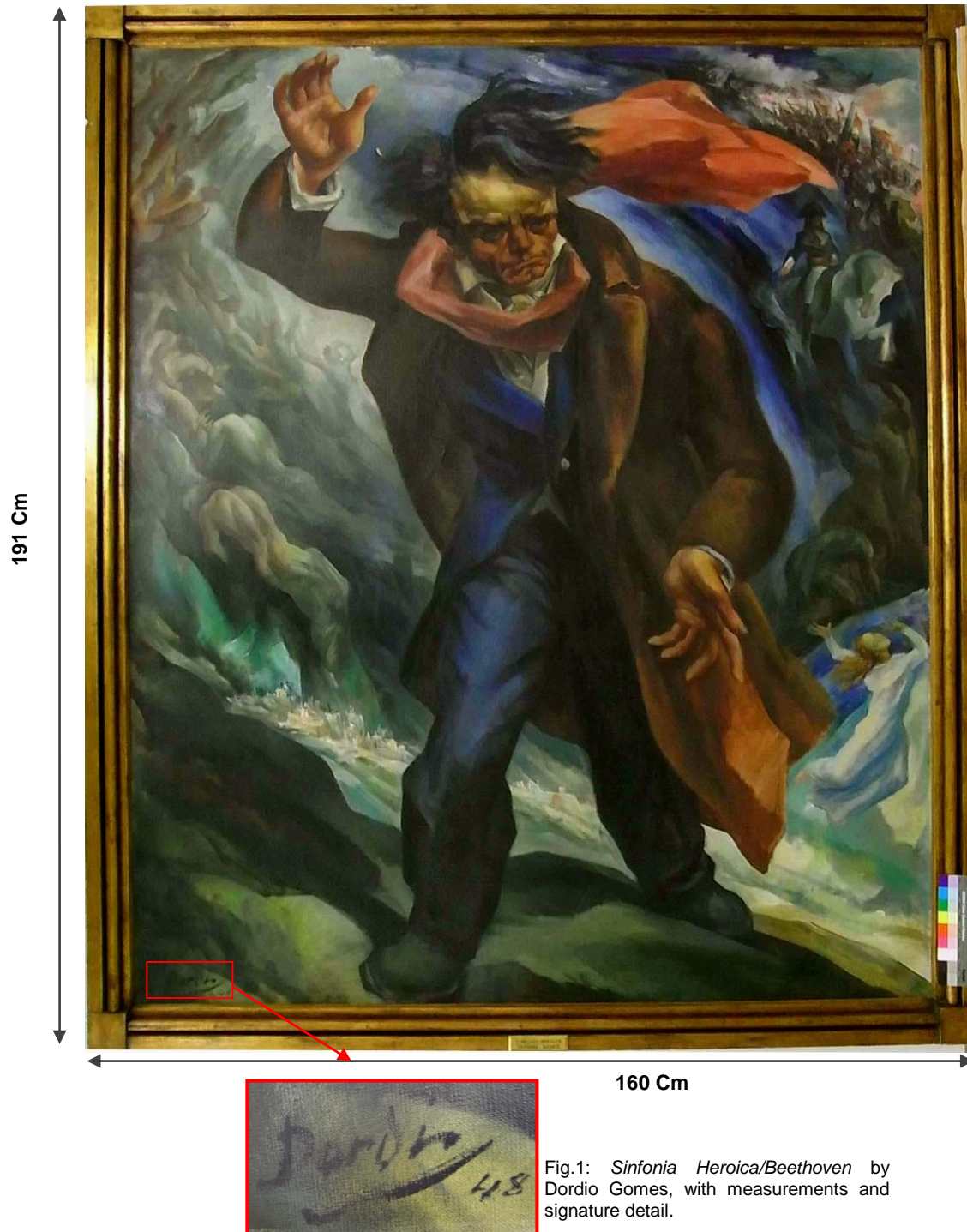


Fig.1: *Sinfonia Heroica/Beethoven* by Dordio Gomes, with measurements and signature detail.

CHAPTER II: INFORMATION ON THE ARTIST AND HIS CONTEXT

II.1 ARTIST BIOGRAPHY

Dordio Gomes was born 26 of July 1890 in Arraiolos and died in 1976 in Porto. At the age of 12, he enrolled in the Historic Painting course at the Fine Art Academy (Academia de Belas-Artes) in Lisbon where he attended until 1910 [2]. Here, among others, he had Luciano Freire as his drawing Master and Veloso Salgado has his painting Master [3]. Even though the latter instructor had a significant influence on him, it was Columbano's style, and his dark painting tones that influenced him the most during this period [3]. In 1910 Dordio won a Valmor scholarship to Paris, where he worked at the Julien Academy for a few months

until his scholarship was suspended due to issues with the Portuguese Minister in Paris, João Chagas. Although he was in contact in Paris with other artists, such as Santa-Rita and Eduardo Viana (from the Portuguese Modernist movement), Dordio's painting style during this period, appears unchanged [3]. From 1912 to 1920 he lived in the Alentejo, each year presenting his "traditional regionalist" [4] paintings in Lisbon, at the Sociedade Nacional de Belas-Artes exhibitions (SNBA). In 1921 his scholarship was renewed and he returned to Paris, where he worked during 1921-1922 at the École Nationale Supérieure des Beaux-Arts and at Ferdinand Cormon's Atelier [4]. This second period in Paris was decisive for Dordio's work: contact with other artists (e.g. Diogo de Macedo and Abel Manta), artistic movements and visits to other countries (Italy, Switzerland, Belgium, Holland and Spain) allowed him to progress and gave his work a modern style [3]. Leaving behind traditional naturalism, Cézanne became his major influence: in colour and form. Gomes's best-known works are dated from this period: *Casas de Malakoff*, *Auto-retrato da Natureza Morta* (see fig. 2; Ap. II).

In 1922, he participated in the Rio de Janeiro International Exhibition where he won a gold medal.

In May 1923, he took part in the group *The Five Independents* together with Diogo de Macedo, Alfredo Migueis, Henrique and Francisco Franco. They were exhibited at Sociedade Nacional de Belas-Artes (SNBA) which was, according to José Augusto França, the first manifestation of the modernist movement in the 1920s. The *Five Independents* stated: "we are independent from everything and everyone...constructive and expressionist, we don't make a school, we make a choice..." [5].

After returning to Portugal, he stayed in Arraiolos for 6 years. During this period he developed his 3rd painting phase, returning again to regionalist themes (Alentejo landscapes, cork trees and horses) but with a completely different formal and colour treatment from his 1st paintings: now there's a greater influence of Cézanne [3].

In 1932 Gomes had his first solo exhibition at the SNBA and in 1933 he accepted the post of painting professor at the School of Fine Arts of Porto (ESBAP), a post he left only when he retired in 1960 [4]. In Porto, Dordio's work started a new phase where the strong and bright Alentejo coloured palette gave way to a characteristic Porto light: smoother and more diffuse. During his years in Porto he also dedicated a great deal of his work to fresco paintings. In 1937 he participated in the International Exhibition in Paris, receiving a gold medal, and in 1938 he attended the International Exhibition of New York. In 1944 he did his first major mural painting, which consists of two decorative panels at the Rialto Café, Porto. In 1950 he participated in the XXV Venice Biennale and in 1951 and '53 the II São Paulo Biennale [4].

At the ESBAP he taught artists such as Fernando Lanhas, Júlio Pomar, and Nadir Afonso but was Júlio Resende who was the closest to him, initially as his apprentice and later, as a colleague [6].

II.2 DORDIO GOMES WORKING METHOD

II.2.1 INTERVIEW WITH HIS SON, ARCHITECT DORDIO GOMES²

The first contact with the painter's family was through Facebook, initially with his great grandson, André Dordio Gomes and afterwards his son the Architect José Dordio Gomes. An e-mail was sent to the Arch. with questions related to his father's technique and materials which was answered back on the 23rd of April 2010 (see Appendix I: Letter by Arch. Dordio Gomes).

² Parts of the meeting were audio recorded and are included in a disk file along with the thesis.

A meeting with the Architect José Dordio Gomes was held on the 1st of June, 2010 at his home in Porto and was accompanied with his wife, M^a Manuela Dordio Gomes and Dr. Ana Paula Machado (curator at Museu Nacional Soares dos Reis (MNSR)).

At his home, one can observe several paintings, studies and drawings by Dordio, as well as his painting materials: pallets, painting boxes, paint tubes, brushes, tacks and pliers (for images, see appendix II).

As a huge admirer, his son has collected reproductions of his father's pictures and any journal articles, books and catalogs related to the painter.

The meeting was conducted as an informal conversation, where various aspects of the painter's life and work were discussed. The main focus was on questions concerning the artist's materials and techniques and in particular, the work *Sinfonia Heroica*.

ABOUT THE ARTIST PAINTING METHODS:

Regarding his father's painting methods, the architect said that he liked to paint alone in his studio: "for him, to paint was not an easy process; (the painting) was made in anger. I witnessed it, it was a struggle he had with the painting and it was wonderful! He argued with himself. That is the reason why he did not want anyone near him when he was painting: The fight was between him and the painting" (All translations by D. Conde)

Given his manner of working, the son explained that his father didn't have any assistants, but that the person who had worked closest with him was "Master Júlio Resende, [who] was his student at the ESBAP and later, his colleague; they both had a great affinity for one another. Architect Dordio Gomes said that, "before starting the paintings, he studied them with drawings [and] studies and investigated the characters he was going to characterize..." he continued, "one thing that he always cared about was the *composition*".

The Architect said, "when he started a painting, he applied the paint on the palette, then put a bit of oil in the metal container (linseed oil), and then diluted the paint just to make the sketch on the white canvas. So to speak, he drew directly with the oil paint the contours and then covered the space with colour: he did the outline and then filled..."

"My dad had a great facility to draw horses. The last drawing he did was a horse, I witnessed that and was a very big drama when he realized that he had no strength in his hands, that was sometime in the 70's".

ABOUT THE ARTIST'S MATERIALS AND TECHNIQUES:

When asked if his father used to prepare his own canvases, Architect Dordio replied that "He used to buy the white canvases" which likely means that the painter bought the canvases already prepared with a commercial ground layer. He bought the primed canvas at a specialized art store in Porto (Papelaria Modelo, lg. dos Loios) and sometimes in Casa Ferreira (Lisbon). The stretcher bars were often bought by the painter, "there was a house where frames were made and then he stretched the canvases himself. He used tacks to attach the canvas to the stretcher



Fig. 2: Dordio Gomes painting box

and he also used little cardboard squares between the tacks and the canvas to protect it, yes, he had patience to do it!" (See Appendix III; fig.11)

The Architect still owns a wooden box for painting (Fig. 2, above) that his father used: The box contains several paint tubes (10 by Winsor and Newton made in England; 8 *Rembrandt*, label, by Talens, made in Holland; and 1 by Lefranc). He stated that "...the (Lefranc paint tube) must still be from when he was in Paris (before 1922)". Inside the box there were also 13 brushes all from Winsor and Newton from the store Casa Ferreira (each brush has a store mark) and a Pallet (see Appendix II; Fig 3, 4, 5 and 6).

Regarding the brushes, the Architect Dordio said his father kept them in really good condition always cleaning them with soap and water after using.

Regarding whether the artist applied a protective coating or varnish, the architect don't remember if his father had applied one.

ABOUT THE PAINTING "SINFONIA HEROICA/BEETHOVEN":

The Arch. stated that this was a work commissioned by Eng. Sebastião Perdigão who lived in Arraiolos and whose family was good friends with the painter. Sebastião Perdigão "placed the order, asked my father to do a painting of *Beethoven*, because he was very fond of music...Eng. Sebastião had a big room in his mansion in Évora dedicated to music, and it was where this painting stood. It was in this room where my father listened to the 8th Beethoven Symphony for the first time before starting the painting".

The Architect continued, "There are two more studies for this painting, described in the book *Dordio Gomes: Pintor Alentejano* by Celestino David, one that is here [at the Arc. Home] made in wood, and another one with other dimensions (55x43 cm) that Eng. Sebastião had".

After close observation, it was confirmed that the study of the painting that Dordio's son owns, is painted on plywood, measures 40x32 cm and is very similar to the final painting: the formal aspects, the figures represented, the colours and even the impasto areas. It is signed and dated (See Appendix I; Fig.1). About the painting's name, the Arch. said that it was originally called *Beethoven* and not *Sinfonia Heroica* (one of Beethoven's musical scores) because "if you see, this painting is more than Heroics Symphony music, it shows the Master, probably the love of his life, the woman at the bottom, Napoleon and his troops, and notice the horses on the left side of the painting that my father enjoyed painting so much."

CHAPTER III: EXAMINATION REPORT³

3.1 THE AUXILIARY SUPPORT (STRETCHER)

The auxiliary support of a canvas painting (in this case, the stretcher) is an important element as it can contribute or detract from the structural stability of the painting. It is the underlying skeleton which holds the fabric support under tension, thus maintaining the paint composite (preparation layers, paint and coating layers) in plane. For that reason, the image layers rely on the stretcher and its state of preservation.

Sinfonia Heroica's stretcher measures 178x147 cm, and has central cross bars. The stretcher bars measure 7 cm and the cross bars are 9,5 cm wide. The external thickness of the stretcher is 2 cm and the internal thickness is 1,7 cm, which indicates that the frame is bevelled (see Ap. III; Fig 10: scheme).

³ See examination mapping; Appendix IV.

The stretcher joins are squared mortise and tenon, which has the disadvantage of creating gaps as the corner joins open. There were no keys present with the stretcher.

Close observation of the bottom horizontal bar indicates previous wood boring insect damage (6 exit holes associated with xylophagous attack).

The canvas is attached to the stretcher bars with a total of 56 metal tacks, 53 of which were protected with a cardboard square (see fig. 11; Ap. III). The interval between each tack was approximately 10-14 cm, which at the time of this treatment, was seen to be insufficient to hold the canvas evenly on the stretcher.

The vertical cross bar has a paper label fragment (see Ap. II; Fig. 8). Along the edges there are several pencil and pen inscriptions regarding the fit of the bars (see Ap. III; Fig. 9).

It was determined that the stretcher bar is in good condition overall and has appropriate dimensions for the structural stability of the canvas.

3.2 EXAMINATION OF THE FABRIC SUPPORT

The canvas is a single piece with total dimensions of 196 x 153 cm (including the tacking margins). There are no selvedge edges. The fabric overall appears to be strong, although some degradation is apparent because there are two small tears which points to some degree of weakening.

The fabric exhibits a plain weave (1:1). The warp runs vertically with an average 10 fibers/cm, while the weft is in the horizontal position, averaging 11 fibers/cm (measured in 5 different places: the 4 corners and 1 in the middle). The weft was determined by the way it undulates above and below the warp, which is tighter (see Fig. 12; Appendix III). The canvas has an open weave and the fibers have a Z twist. Their overall mechanical strength appears to be high.

Observation of the reverse of the fabric underneath the stretcher bars compared to exposed areas revealed that the colour of the exposed area appears slightly darker, likely due to the presence of particulate matter (dust and dirt). The fabric has two small tears (in the 1st and 7th section) probably caused by mechanical impacts. In both cases, the mechanical impact caused bulges around the impact area (see Fig. 13; Ap. III).

The major instability observed in the painting is related to extensive out of plane distortion (deformation) associated with both the paint composite and the fabric support. There are various deformations associated with the support: along the edges, one can observe an undulation of the fabric support that follows the tack intervals on the tacking margins (see fig. 18; Ap. VI). In the center of the painting, one can observe the bulging that coincides with colour areas on the painted surface (see fig. 20; Ap. VI). As well, the canvas is very slack on the stretcher, possibly in part, due to the absence of keys which could have been used to expand the stretcher and thereby tension the fabric. The observation of the painting with raking light clearly reveals the extent of the severe deformation in the paint composite/canvas (see fig 18 and 19; Ap. V).

3.3 EXAMINATION OF THE PAINT COMPOSITE

3.3.1 SIZING LAYER

The existence of a sizing layer, the way it has been applied and the material used is of great importance to a painting's structural stability as the state of the size layer will dictate to a large extent, the painting's susceptibility to changes in Relative Humidity (RH) and to moisture and water-based treatments [7]. And the precise location of the size layer is a matter of great importance [7]. If a size layer is applied in the form of a

gel (at room temperature), it will form a layer on top of the fibers as a coating but will not penetrate them. When subjected to moisture, this discreet size layer will allow the fabric “to develop its full shrinkage potential while, at the same time, acting as a release layer for the ground” (Hedley, 1989) [7 p.115]. When the size layer is applied as a liquid, it penetrates into the fibers. In this case, according to Hedley’s research, reducing the shrinkage of the fabric as well as enabling the ground layer “to key onto the yarns more securely” [7 p.115].

3.3.2. THE GROUND LAYER

A ground or preparation layer is applied to most painting supports. The ground ensures adhesion of the paint layers to the support and provides the desired texture, and in some cases, the undertone for the image layer/s [8].

Sinfonia Heroica features a light coloured, whitish ground layer which has been applied evenly to the canvas and uniformly covers the tacking margins. Application marks (e.g. brushstrokes, streaks, etc) are not visible, and judging from the uniform coating of the tacking margins this is most likely, a commercial priming [6].

The ground appears to be in good condition, showing good adhesion to the fabric (capacity to stay adhered to the substratum) and with good internal cohesion (intramolecular attraction) [9], with the exception of the tacking margins, where there is some cracking and poor adhesion associated with the turn-over edges and the cut-edge of the fabric.

3.3.3 UNDER DRAWING

Infra-red (IR) photography did not show evidence of carbon containing under-drawing, however the dark lines around the figures are likely done with brush and paint. A visible fragment from the graph used in squaring-up could be in pencil (see fig. 31; Ap. VII). This is consistent with what Arc. Dordio said about his father’s technique: “the first sketch was made with paint and brush” [6]. Since IR photography can only reveal under drawing when the subsequent layers are transparent to IR wavelengths (9 p. 51), a preliminary drawing done in washes with paint similar to or the same as that used in subsequent layers would not be detected.

3.3.4. PICTORIAL LAYERS

The painting presents an overall thin paint layer application that can be best observed with transmitted light (see fig. 17; Ap. V). In some areas, the painting layers were so dilute that is possible to observe the white ground underneath, however, in other areas (Beethoven’s face, and the troops) the paint application is much thicker. On the face, the thickness is due to an overlap of paint layers, associated with redoing the figure’s face repeated times (an aspect reported by Dordio’s son), while in the area of the troops painting area, the thickness is due to heavy paint brushstrokes (*impasto*).

The paint presents several conservation problems: The most severe is the weak adhesion between paint layers (which is observed in several areas where two or more layers overlap: mainly situated in the 1st and 2nd sections). This interlaminar cleavage may, in some cases, be related to a previous mechanical impact (signs of which are evident as scrapes on the surface leading to the impact area) (see fig. 34 and 35; Ap. VIII). In these zones, the upper paint layer has already detached from the surface leaving the bottom layer exposed. Of significant concern for the long term stability of the painting, are other areas of delamination where the uppermost paint has flaked off, with no signs of mechanical impact. This suggests that the painting

suffers from “inherent vice” which points to a fundamental weakness within its structure due to materials or application techniques (fig 7, above).

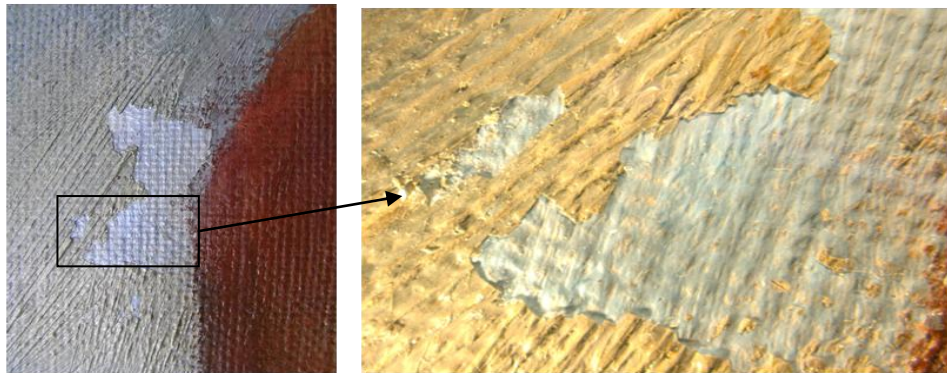


Fig. 3: Detail of *Sinfonia Heróica*, 1st section near figure's hand. Interlaminar cleavage: the upper paint layers have already detached from the surface.

Besides the interlaminar cleavage problems, the painting also presents small irregular drying cracks probably due to the fast drying of the binder in the brown area, Beethoven's left shoulder (see fig. 25; Ap. VII); Impact marks and abrasions on the upper layers are found at the bottom (see fig. 28; Ap. VII); Abrasions on the bottom and edges of the painting appear to be caused by the frame where it contacts the paint surface (see fig. 27; Ap. VII); Paint has been transferred from the frame at the right bottom edge (see fig. 28; Ap. VII).

3.3.5 SURFACE COATING

The surface of the paint layers exhibits an uneven appearance, in some areas, the varnish shows an even high gloss, while in others; it has a matte appearance (see fig. 9, above). This appears to be related to the unevenness of its application which is clearly visible under UV light (fig. 10, above; and fig. 24; Ap. VI). This surface coating shows a light green fluorescence which, in some areas, fluoresces very brightly (consistent with the higher the density of the varnish layer) while in others, there is little fluorescence (consistent with a very thin varnish layer). In the dark areas of the painting (for e.g. the figure's suit) it is easier to observe the brush strokes of the varnish application. In the light areas of the painting, possibly due to the amount of zinc white present (see chapter V; 5.6: the role of zinc), the fluorescence is high but seems to also be coming from the pictorial layers (see fig. 22; Ap. VI). Overall the, surface coating, appears to be very thin.



Fig. 4: Uneven varnish that cause differences in the paintings gloss and colour saturation.



Fig. 5: UV photography showing uneven varnish application.

After removal of the frame, it was possible to see that the edges did not exhibit fluorescence indicating that the varnish was applied after framing (See fig. 23; Ap. VI). Since there is no evidence of past conservation treatments, the current varnish layer may well be the first varnish applied.

In the dark tones of the figure's face (around the nose and mouth), where the paint is heavily applied, a *blooming* effect was observed. Bloom refers to, "a cloudiness on the shining surface" [11] which can appear as a whitish waxy-looking deposit (see fig. 30; Ap. VII).

In the 8th section, drips and runoff deposits can be observed. This appears to be a brown transparent polymeric material, perhaps concentrated varnish (see fig. 32 and 33; Ap. VII). On top of the varnish layer, accretions associated with insect excretions (fly specks), can be observed (especially on main figures forehead) (see fig. 29; Ap. VII).

Since there is no evidence of recent treatments, it is likely that the varnish is original, possibly applied by the artist.

CHAPTER IV: MICRO LEVEL EXAMINATION⁴

4.1 TEXTILE FIBER IDENTIFICATION

The fiber identification for the canvas support was made by observation of a sample of yarn removed from the edge of the right tacking margin.

The fiber's longitudinal section, shows a regular circular shape, placed parallel to each other (fig. 6; below). The longitudinal section presents points of transverse displacement (see fig. 6) at frequent intervals along the fiber (Hall). The elementary fibers are similar to flax (*Linum usitatissimum*) or hemp fibers (*Cannabis sativa*) on their size and overall appearance. In longitudinal view both types of fibres exhibit frequent joints as well cross-striations and fissures [12]. To distinguish between both fiber's, it's necessary to observe the fiber's cross-sections through the optical Microscope (OM) (fig. 7; below).

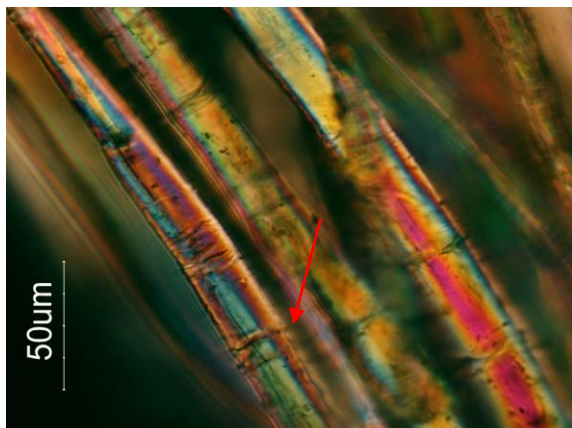


Fig. 6: Optical Microscope (OM) Longitudinal view (40x) image of the canvas fibers in visible polarized, transmitted light. The arrow indicates the dislocation points [40].

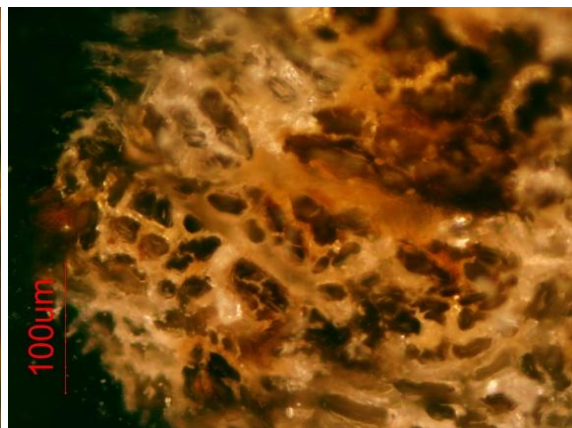


Fig. 7: cross-section of the canvas support fibers. 20x amp. Dark field polarised light

In cross-section, hemp fibers have a spindle-like shape and polygonal (mostly pentagonal) cells with rounded edges. They are also uneven in diameter, and show a channel (lumen) inside the elementary fiber [13] (as shown in figure 7 above). The properties of hemp are such that canvases made with this kind of fabric can

⁴ See Appendix IX for identification of the sampling areas and Appendix X for Instruments and methods.

be coarser than canvases made with flax. Apart from flax, hemp has been the most widely used fabric for canvas making until the XIX century but one of its disadvantages is that it maintains deformations which can complicate treatments to remove distortions in the fabric [14].

4.2 SIZE LAYER STAINING: IDENTIFICATION OF PROTEIN BASED SIZE LAYER

As noted above (Chapter III: 3.3.1), the location of an animal glue based size layer, either within the canvas fibers (impregnation due to fluid application) or on top as a discrete layer (gel application) has great importance in relation to the treatment options [15]. These differences will result in a very diverse reaction of the painting to variations in humidity [16] and are connected to the physical stability of the paint layers: when water is absorbed by the canvas causing an initial softening in the size layer; the softened size acts as a “release layer”, allowing the still brittle paint and ground to fracture and to be pushed out of plane and sometimes off the surface of the canvas due to the shrinking canvas [16].

To identify the existence of a protein based sizing layer, a protein staining technique was carried out on a cross-section prepared with a sample taken from the edge of the right tacking margin and viewed under OM. To verify the location of the size layer on or within the fibers of the *Sinfonia Heroica* sample, 3 different samples with a known method of application of size layer prepared by for the HART Project [17] were used for comparison. These 3 HART Samples were identified as D2gCSO; D2fCSO and D2nCSO and were also prepared as cross-sections. Each HART sample had the same canvas support and a first ground layer composed of chalk and lead white in oil. Sample D2gCSO, had a size layer made with alum-tawed hide-glue applied with a spatula in form of a gel; sample D2fCSO had the same size, but it was applied with a brush in the form of a fluid; Sample D2nCSO did not have any size applied.

For the identification of the size penetration, a protein staining technique (using a non-covalent UV fluorescent dye) was used [18]. The stain was applied to each cross-section and in about 15s started to react, showing an orange fluorescence under UV light if the protein identification was positive. As seen in (see fig. 37, 38 and 39; Ap. XI), each application method (fluid or gel) showed a different degree of protein impregnation on the canvas fibers. While in the gel size layer (fig. 38; Ap. XI) the protein stayed on top of the fibers, with the fluid size layer (fig. 39; Ap. XI), it penetrated to inside the fibers.

Comparing stain results, it can be concluded that in *Sinfonia Heroica*, the protein based size layer is deeply impregnated into the support fibers, likely due to a fluid application (fig. 8, 9 and 10; below)

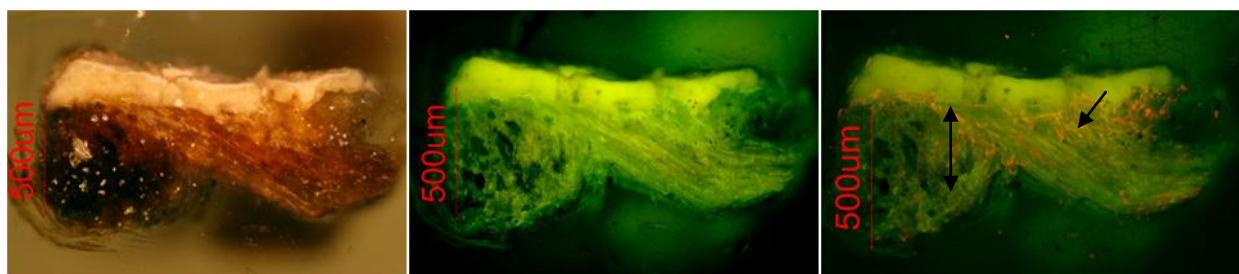


Fig. 8: 5x amp OM images of Cross-section of ground layer and support of *Sinfonia Heroica*.; Visible reflected light; Fig. 9: Visible light, filter set 9:(BP 450-490, FT 510)- Fluorescence; Fig. 10: Visible light, filter set 9, after staining. In this image, one can observe the high level of protein impregnation into the support fibers.

4.3 GROUND LAYER

The Cross-section OM image displayed below (fig. 11 and 12), is representative of the ground layer construction. It shows a ground composed by two layers of different aspect and thickness which corresponds to a commercially prepared “double ground” or a “double priming” [19].

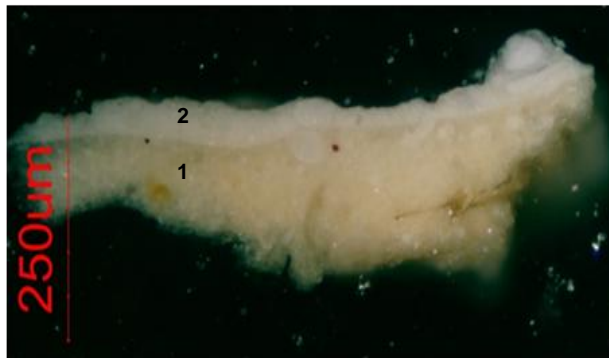


Fig.11: Cross-section of the two-layer (double) ground. OM: dark field; reflected, polarised light 10x mag.

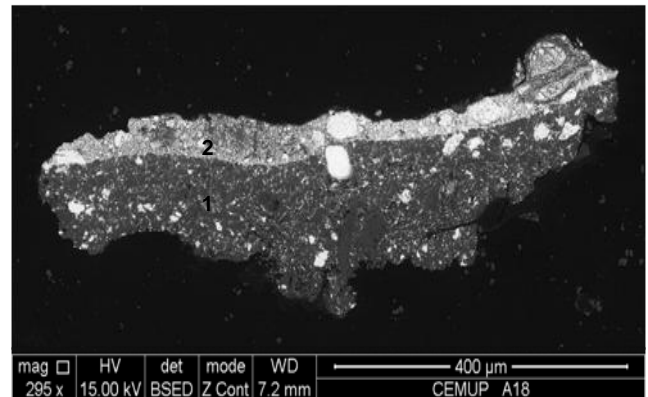


Fig.12: The back scattered electron image of the two-layer ground reveals a chalky bottom layer with some white lead and an upper layer predominantly lead white. (295x mag.).

The bottom layer (identified with nr 1; fig. 11 and 12, above) shows beige, translucent materials, with polygonal shaped white particles of different sizes (from 100 - 150 μm in width). The upper, more solid white layer, (number 2, fig. 11 and 12, above), shows big particles heterogeneously scattered within the white matrix. In comparison to layer 1, layer 2 is much thinner (presenting an aprox. 50 μm width).

The bottom ground layer mainly consists of calcium carbonate with a minor amount of lead white and the top layer consists mainly of lead white with a minor amount of calcium carbonate. The μ-Raman (μ-R) characterization identified calcite (CaCO_3) and basic lead (II) carbonate (hydrocerussite $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) (see fig. 40 and 41; Ap. XIII) which was in agreement with SEM-EDX analyses (fig. 13 and 14; below). The μ-FTIR analyses identified an oil binder for both layers (see fig. 42; Ap. XIII).

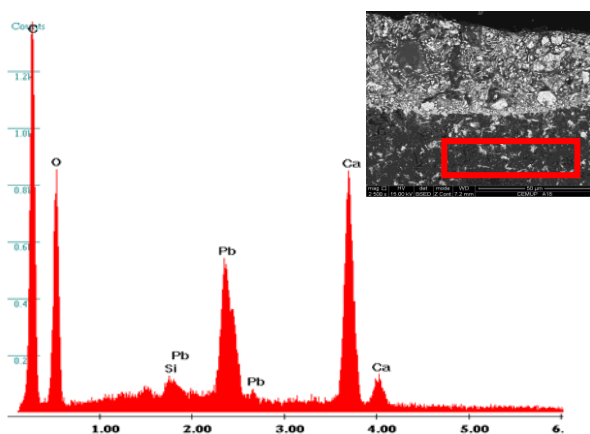


Fig.13: SEM-EDX analyses on the GL cross-section layer 1 where both calcium and lead elements have been identified.

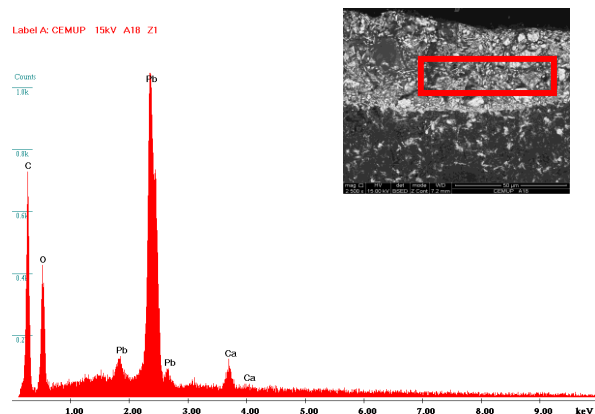


Fig.14: SEM-EDX analyses on the GL cross-section layer 2 where both calcium and lead elements have been identified.

4.4 PICTORIAL LAYERS

In general, all cross-section statigraphies show a thin apparently single application of colour. Even though *Sinfonia Heroica* is a mostly dark toned painting, where light areas aren't prevalent, white colour has been

used to mix with several different paints to lighten the tones.(see Appendix XII: Cross-section identification and analyses).

4.4.1.OIL BINDER

As systematically described by Van der Weer et al [20], IR analysis is a valuable technique to assess the conservation state of an oil binder. The characteristic fingerprint for an aged drying oil includes: 1) the C-H region (2927 and 2855 cm^{-1}); 2) the carbonyl region: original ester ($\approx 1740\text{ cm}^{-1}$), carboxylic acid ($\approx 1740\text{ cm}^{-1}$) and metal carboxylates (1550 to 1400 cm^{-1}). In certain paints, it will still be possible to detect the ester triplet, resulting from the C-O ester bond vibrations [20]. In a degraded varnish, Besides the C-H absorptions, it would also be possible to observe the peaks of the carboxylate formed.

In our study, both in the painting as well as in the paint tube samples, zinc white was ubiquitous (see 4.6: the role of zinc). The Infrared spectra of a 1941 zinc white paint described by Van der Weer et al presents common features also observed in several of our samples: for example the 3 broad unresolved, absorption bands centred at 1589 , 1460 and 1159 cm^{-1} where, the band at 1589 cm^{-1} is the only one assigned by the authors, to the carboxylate absorption; the 1460 cm^{-1} is resolved (by second derivative) as a C-H bend vibration and carbonate absorption; finally, the 1150 cm^{-1} band is attributed to the presence of alcohol groups in the oil, as a result of degradation. A closer examination of the spectra presented by the authors, led us to state that it is possible that the 1150 cm^{-1} absorption. is due to the presence of a sulphate (gypsum). Also the assignment of the 1460 cm^{-1} band to only a C-H bend and carbonate could be incomplete because it's not possible to exclude the absorbance of carboxylate in this region. Based on the above data described it is not possible to conclude if the $1582/1429\text{ cm}^{-1}$ absorbance's are due to metal ion carboxylate formed during aging or added to the paint during its formulation however such are characteristic of a zinc white paint. The IV spectra acquired from the Dordio's paint samples (Fig. 34 and 35 p.20) show $1582/1429\text{ cm}^{-1}$ peaks that can be due to the carboxylate's absorption. However there isn't a database that can help us to confirm whether these peaks are really due to the carboxylates or not.

4.4.2 COLOUR PALETTE

WHITE

Pure white colour was sampled from a thick brushstroke in section 3 near the troops (see Ap. IX: sampling areas). μ -XRF analyses on this colour were performed in 7 different places, all of them indicating the presence of large amounts of Zn (see table 2; Ap. XIV). The μ -Raman analysis of a white colour (micro-sample A9) (Fig. 22), shows the characteristic zinc oxide (ZnO) strong peak at 440 cm^{-1} [21] and suggest the use of zinc white. Although, as it has been observed in several articles, zinc white is a very difficult pigment to detect with μ -Raman and even X-ray diffraction [22] [23 p. 19].

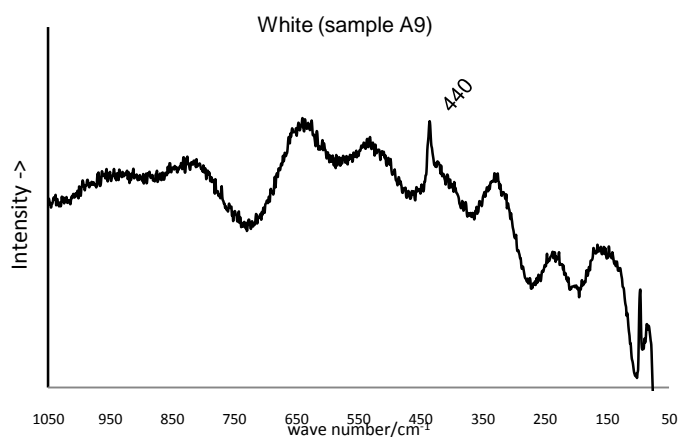


Fig.15: μ -Raman analysis on sample A9 (white brush stroke) show the ZnO characteristic peak at 440 cm^{-1} ($\lambda=632,89\text{ nm}$, 10s, D2).

Cross-sections A1-A1.5, observed through the OM, show one or two layers with white as the main colour. An identical characteristic to all is the bright fluorescence in UV of small particles which is consistent with the fluorescence emitted by zinc or zinc oxide particles [24] (see fig. 43; Ap.: XIII).

BLUE

Different kinds of blues were found in the painting. Cross-section A2 (above) from the sky near the main figure's head, presents several blue and greenish layers, with different morphological and chemical composition. Here, the ridges of paint were built up to a thickness of $\sim 140\ \mu\text{m}$, as opposed to the generally thinner application of paint elsewhere. The paint was applied in up to 9-10 layers, possibly allowing each other to dry before the following was applied.

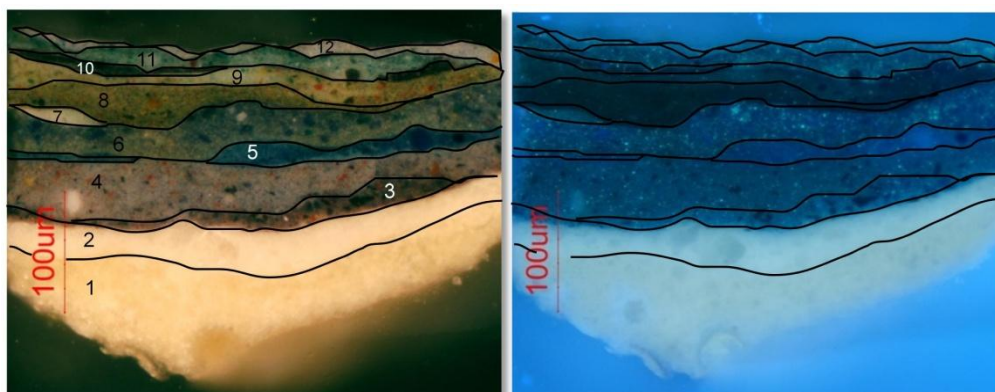


Fig.16: OM of Cross-section A2, removed from the 2nd section, around a lacuna. A: 20x magnification, reflected, polarised light; B: 20x mag., UV light. On photograph A each colour layer is identified with the number 1 to 12.

The μ -XRF analyses of 6 different hues of light blue, and the SEM-EDX done on layer 6 (cross-section A2) (see fig. 44; Ap. XIII), indicates the presence of the elements Al, S, Co, Si (besides C, O, and Zn), most probably due to cobalt blue pigment ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) [25] which were consistent with μ -FTIR analysis on micro-sample 20 (fig. 24, below). Cobalt blue's characteristic IR absorbance is in the lower frequency of the IR region: $\sim 679\ \text{cm}^{-1}$ [26].

Lazurite or synthetic ultramarine blue (introduced c.1828 ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{S}_n$)) (21) was also identified through μ -Raman. In fig. 25, below, it is possible to observe its characteristic μ -R peaks: at $258\ \text{cm}^{-1}$ w.; $548\ \text{cm}^{-1}$ vs.;

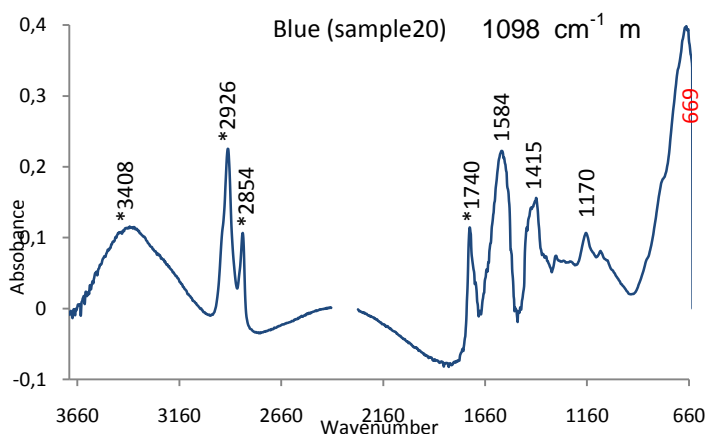


Fig.17: IRSpectrum of blue (Sample A20). In red it's marked the IR absorbance for Cobalt blue pigment [26]. The asterisk marks the oil binder [20] absorbance

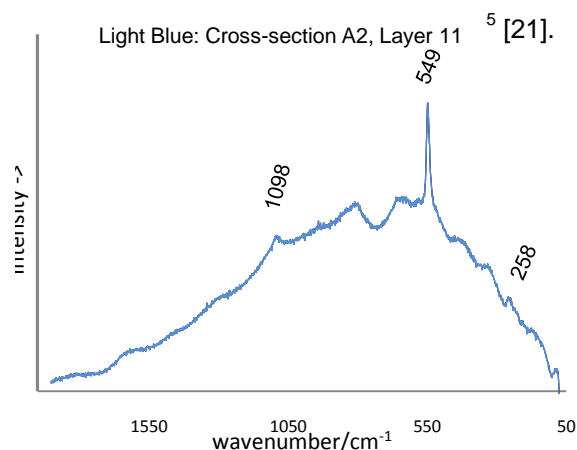


Fig.18: μ -Raman spectra of light blue colour, layer 11, from cross-section II A2 ($\lambda=514,5$; 2 mV; 10s).

⁵ (peaks relative intensity: w=weak; m=medium; vs=very strong).

The Dark blue was identified as Prussian blue pigment (Iron (III) hexacyanoferrate (II) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) either through μ -Raman or μ -FTIR analysis (fig. 26, below). The μ -FTIR spectra for sample 2, show the characteristic absorbance of $[\text{Fe}(\text{CN})_6]^{3-}$ ion stretching band at $\sim 2100 \text{ cm}^{-1}$ [26] and also the cobalt blue absorbance peak at $\sim 669 \text{ cm}^{-1}$ [26]. The paint sample also indicates the presence of calcium carbonate which absorbs $\sim 3406 \text{ cm}^{-1}$ and 1113 cm^{-1} [27].

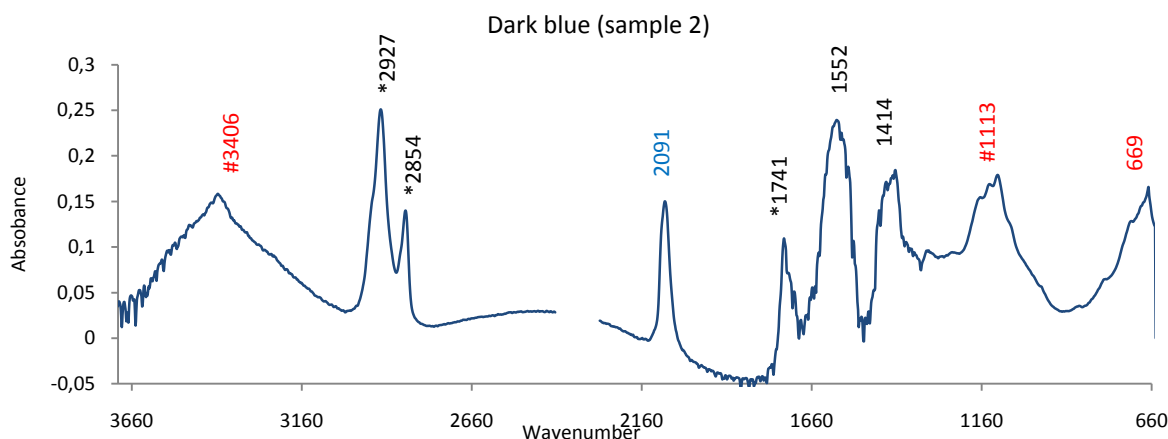


Fig.19: Infrared Spectrum of dark blue colour (sample 2). Marked with blue colour is the characteristic $[\text{Fe}(\text{CN})_6]^{3-}$ ion stretching absorbance band at $\sim 2091 \text{ cm}^{-1}$ [26]; cobalt blue pigment IR absorption [26] is marked with red colour, and the peaks related to the calcium carbonate filler are marked with “#” symbol [27]. The oil binder peak at 1741 cm^{-1} shows that the oil is in good condition [20] and is marked with an asterisk.

RED

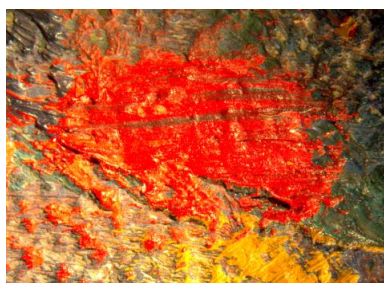


Fig.20: Microscope photography. Detail of red brush stroke used to represent the troops flag, 3rd section.

As it can be seen in the painting, the colour red is mainly used on Beethoven's scarf where is present in several shades, but it can also be observed in the troop's flags. In this case, the brush strokes appear denser and done with pure red paint.

μ -XRF analysis identified Fe, Cd and Se elements related to the pigments (see table 1: Ap. XIII). These elements were also identified together with SEM-EDX analysis on a red particle in a cross-section A1.1 (fig 21, above) and are consistent with the use of Cadmium red pigment (Cadmium sulfoselenide: $\text{CdS}(\text{Se})$) which is a synthetic pigment extensively used in oil paint after the 1940's [25] also present in an oil colour tube in the painter's box, labelled “Cadmium Rouge”, Lefranc (see fig. 57; Ap. XIV).

The μ -FTIR analyses of a red colour (sample 8), shows characteristic absorbance's for magnesium carbonate at $3647, 3441, 1487, 1421, 853$ and 801 cm^{-1} [26] associated with a filler material. The pigment peaks for cadmium red are not visible as the pigment does not absorb in the IR [20].

Label A: CEMUP 15kV A1.1 Z1

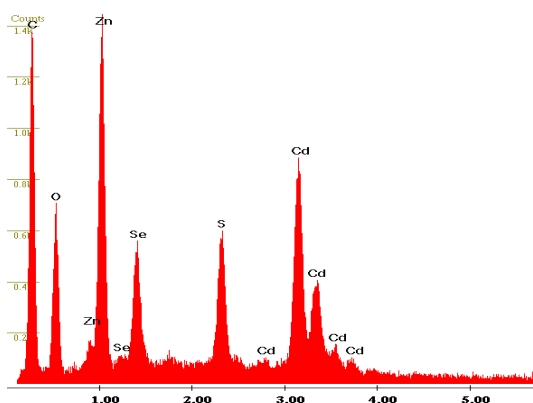


Fig.21: SEM-EDX analysis on red present in cross-section A1.1. The main peak is zinc, but also Cd, Se, S. Beyond C and O.

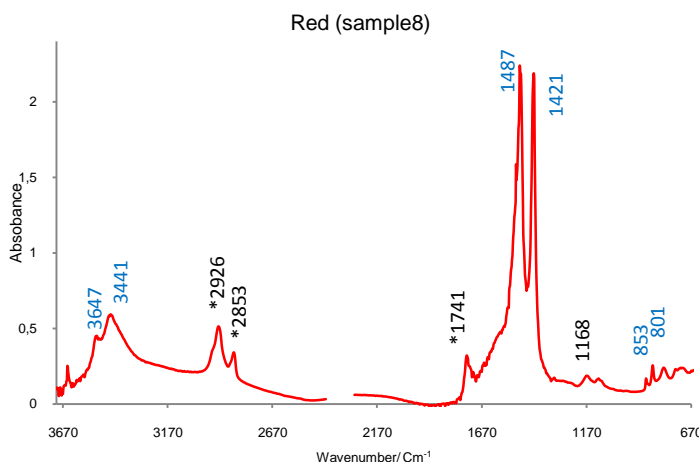


Fig.22: μ-FTIR spectra for red colour (sample 8). Marked in blue, is the IV absorption peaks for magnesium carbonate [26], and with the asterisk, IV characteristic peaks for the oil binder [20].

BROWN

The brown colour and brownish hues are present over a large part of the painting: Beethoven's long jacket, but also in flesh tones and the background. Cross-section A1.3 below, was taken from the edge of Beethoven's hand (top layers of the interlaminar cleavage area) and shows that the brown colour used to paint the hand was applied on top of a grey coloured background which appears white in fig.24. Here it is possible to observe that the brown paint layer is very thin (20-5 μm thickness) and consists of very small particles of mainly brown colour.



Fig.23: OM Picture of cross-section A1.3. 20x, visible light, filter 2.



Fig.24: OM Picture of cross-section A1.3, 20x, UV light, filter 8.

The μ-Raman analyses of cross-section A1.5 (fig. 25, below) indicates the presence primarily of synthetic Iron (III) oxide, Fe_2O_3 which is marked with red colour [21]. Therefore, the pigment is likely Mars Red; a Synthetic Iron (III) which appeared in the artist's palette in the XIX century [25].

μ-FTIR analyses of red (fig. 26, below) identified the Si-O-Al characteristic absorbance peak from kaolinite [28] suggesting a red ochre. μ-XRF analysis detected Mn, along with Fe and Si elements, which points to the presence of Raw Umber or Burnt Umber ($\text{Fe}_2\text{O}_3 + \text{MnO}_2 + \text{clay}$).

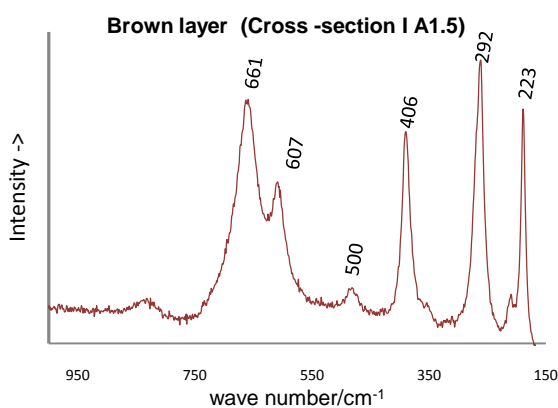


Fig.25: μ -Raman Spectrum of brown layer in Cross-section A1.5. ($\lambda=632,8$, 10s, D2) showing the characteristic peaks for Mars red [21].

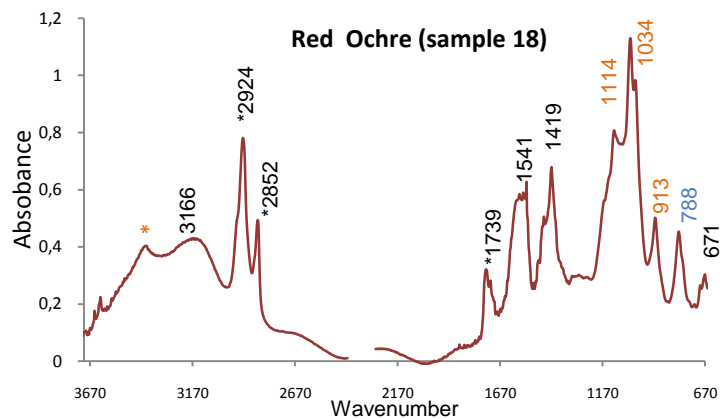


Fig.26: μ -FTIR Spectrum of the brown colour (sample 18). the Si-O-Al absorbance peak of kaolinite [28] is marked with orange color is marked. The blue color marks the hydrous ferric oxide[28]. The peaks related to the linseed oil binder IR absorbance [26] are marked with a black asterisk.

GREEN

Green colour predominate through the painting, particularly in the background and foreground. Two cross-samples removed from different green painted areas show rather different kinds of paint. Cross-section A7, removed from the edge of a lacuna, shows a very thin saturated homogeneous green layer, while A5, removed from the right edge of the painting shows a light green layer of about 40 μm thickness intermixed with brown.

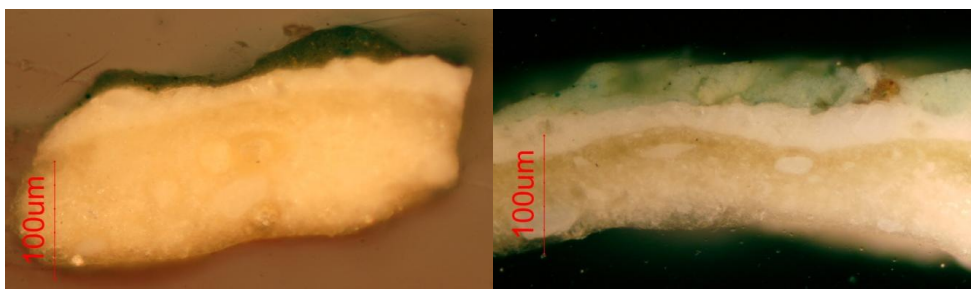


Fig.27: OM obs. on cross-sample A7, 20x mag.; dark field visible, polarized light.

Fig. 28: OM obs. On cross-sample A3, nearby green lacuna area. 20x mag.; visible polarized light.

The μ -XRF analyses done on 9 green coloured areas all indicate the presence of Chromium (Cr) element pointing to the possible use of Viridian ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) or another chrome based pigment such a chrome oxide. However it's characterization wasn't possible with IR analyses because chrome oxide (Cr_2O_3) does not absorb in the IR [27 p. 19]. Yet, analyses done on Dordio's Talens/Rembrandt's paint tube "Permanent Green L" show the same IR characteristic absorption peaks (see fig 55; Ap. XV) and μ -XRF analyses also indicate the presence of Cr (see table 2; Ap. XIV).

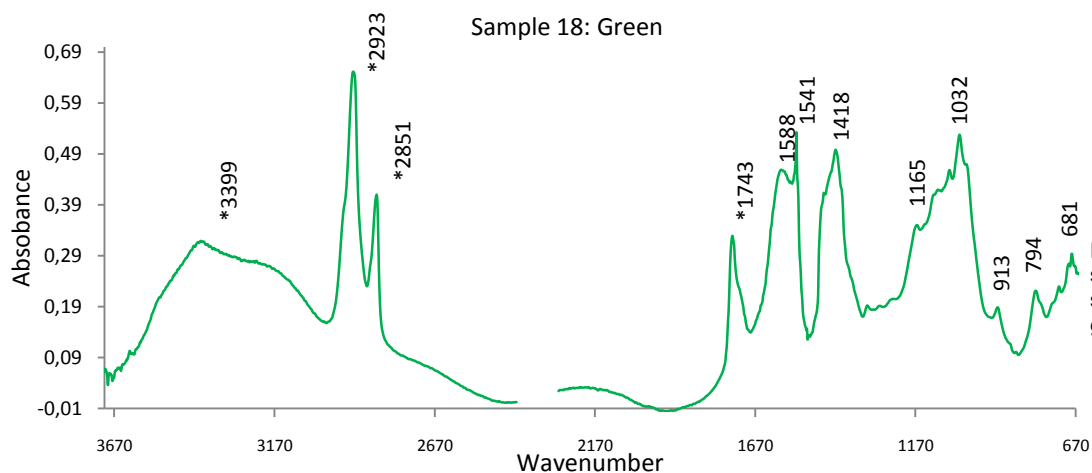


Fig. 29: μ -FTIR spectra for sample 18, light green.

YELLOW

Yellow tones are not predominant in *Sinfonia Heroica's* composition; in fact, there is only one minute detail where a single yellow brush stroke is visible (section 3, in the troop's flags) (Fig. 30)

μ -XRF analyses on this area indicate the presence of Fe and Cd. With μ -Raman analyses on sample 6 it was possible to identify synthetic iron (III) hydroxide, $\text{Fe}(\text{OH})_3$ (Mars Yellow) [30] which is also in accordance to μ -FTIR analyses of the same sample. The calcium carbonate identified is normally only associated with the synthetic pigment [26]



Fig. 30: microscope image of the yellow brushstroke, 3rd section.

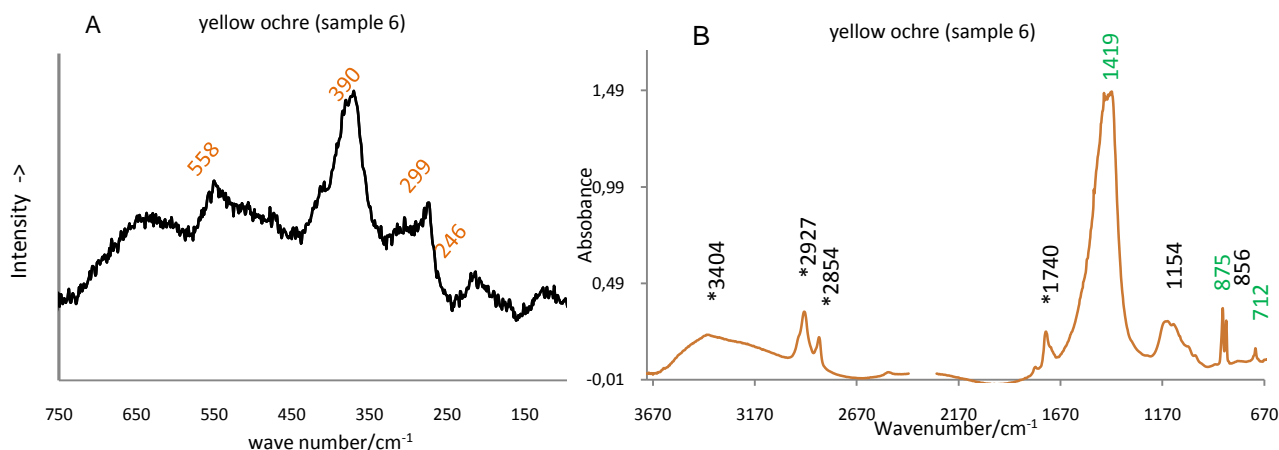


Fig.31 A: μ -Raman Spectrum of sample 6 (yellow colour) showing the characteristic peaks for Mars yellow [21]. Fig. 31 B: IV Spectrum on a yellow colour (sample 6). The characteristic calcium Carbonate absorbance's [26] are marked with green color The peaks related to the linseed oil binder IR absorbance [26] are marked with black asterisk [28].

BLACK

Black was identified through μ -Raman on cross-sample A4 showing characteristic carbon black bands: 1587 cm^{-1} and 1329 cm^{-1} [21] (see fig 46; Ap. XIII). The OM observation of this cross-section shows a very thin single layer of paint (less than $30\text{ }\mu\text{m}$) on top of the double ground. The paint layer shows very dark small particles that can't be distinguished under visible light, although it's possible under UV light to identify the existence of zinc (very small fluorescent particles fig.32). These particles can be due to a deliberate mixture of black and zinc white paint by the artist but can also be due to the addition of zinc to the paints by the colour maker (see 4.6: the role of zinc).

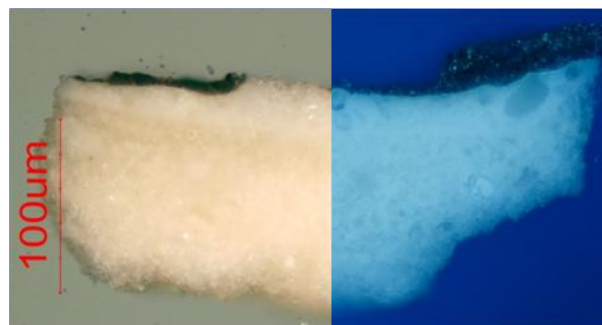


Fig. 32: OM Picture of cross-section IV A4, 20x mag.; 1st half: visible polarized light 20x, UV light, filter 8. 2nd half: UV light

4.5 VARNISH

Even though the varnish layer wasn't very visible in the cross-sections analyzed, a micro-sample removed from the painting surface, indicates the use of a surface coating based on triterpene resin: which points to the use of Dammar or Mastic varnish. The characteristic IR bands of Dammar are: 3600-3200 cm^{-1} O-H str. bands; 3100-2800 cm^{-1} C-H str. bands; 1740-1640 cm^{-1} C=O str. bands; 1650-1600 cm^{-1} C-C str. bands; 1480-1300 cm^{-1} C-H bend. bands and 1300-900 cm^{-1} C-O str.

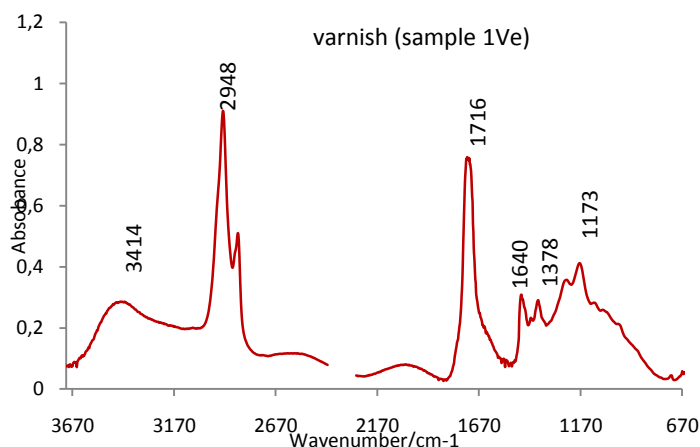


Fig. 33: μ -FTIR spectrum for Varnish sample 1Ve showing the characteristic absorption peaks of a triterpene resin.

band [27]. The varnish has been applied in a very thin coating, and is not considered to be unduly coloured or cracked. Therefore varnish removal is not considered warranted at this time.

4.6 THE ROLE OF ZINC IN THE PAINT LAYER DELAMINATION

The IR analyses made of paint samples removed specifically from the interlaminar cleavage area (Sample 10 and sample 11, respectively top and bottom layers of the interlaminar cleavage area) indicate presence of zinc white. Zinc is thought to influence the aging of oil in different ways: it stimulates the formation of alcohol groups, catalyses the hydrolysis of glycerol esters, and forms metal carboxylate with the carboxylic acids present [20].

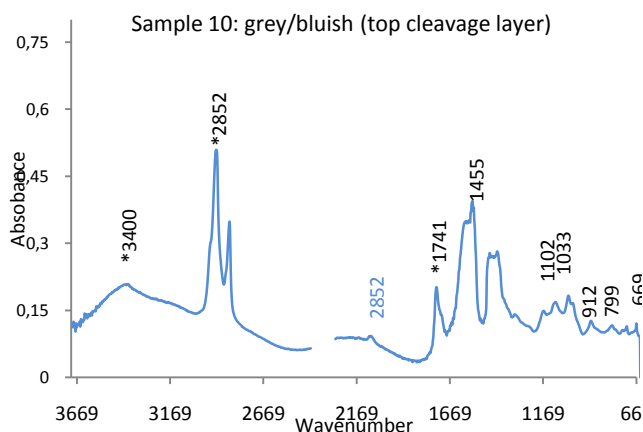


Fig.33: IR spectrum of sample 10, top layer of the cleavage area. The characteristic absorbance of C=N Prussian Blue ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$) [26] is marked with blue colour. The peaks related to the linseed oil binder IR absorbance [26] are marked with black asterisk's.

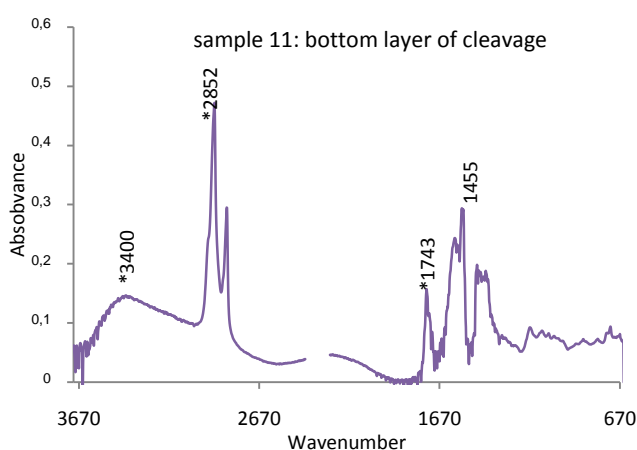


Fig.34: Spectrum of sample 11, the bottom layer of the interlaminar cleavage area.

As noted almost every μ -XRF analysis of the painting, along with OM UV fluorescence observation of the cross-sections of the interlaminar cleavage areas, the presence of zinc elemental is very strong (see fig 58 and 59; Ap. XVI).

Current research suggests that a wide variety of metal ions, including zinc, are affecting the ultimate film formation of oil paints. As studied by Mecklenburg, Tumosa and Vicenzi in the article *The influence of pigments and ion migration on the durability of drying oil and alkyd paints*, "a layer of paint with zinc oxide

can cause all adjacent paint layers to either become brittle when normally they would dry to a taught durable film or alter the drying characteristics of adjacent paint layers” [31]. Zinc also promotes an increase in paint transparency as well as increases brittleness and efflorescence [32].

It's known that materials other than pigments and oil, were often added to colours by paint manufacturers. The addition of metallic soaps, such as zinc stearate as stated in Ralph Mayer's book *The Artists Handbook of Materials and Techniques*, “will result in good buttery pastes. When added in very small amounts, there is probably little danger of any harmful effect on the structural strength of the resulting film. If used in sufficient quantity, the metallic soaps will tend to cause the oil film to become spongy and to get brittle with age”[33]. Generally, metallic soaps are compounds of alkaline earth metals or heavy metals and monobasic carboxylic acids of 7 to 32 carbon atoms and their water insolubility differentiates metallic soaps from ordinary soaps [34]. In the manufacturing world, metallic soaps can be divided into two groups: paint driers, and modifiers of consistency, gloss or other properties. Zinc soaps can be used for both [34]. However, aside from of being added to the paint deliberately metal soaps can also result from by a reaction between the oil medium and metal ions present in the paint. These metal ions are most commonly lead- and, more recently, zinc-containing pigments or additives. The zinc containing pigments, driers, or extenders react with the fatty acids to form zinc soaps. In some cases, the pigment particles react away leading to saponified regions, which can grow further, swell and finally protrude through the paint surface [32].

The possibility was considered that zinc soaps could have migrated to the interlaminar areas in Gomes's painting resulting in separation or interlaminar cleavage. Note the very bright layer of the cross –sections seen in UV light (see fig. 43; Appendix XIII and fig. 61,62 and 63; Ap. XVI: Interlaminar cleavage).

Another hypothesis for the cause of interlaminar cleavage is the high pigment volume of zinc oxide pigment related to the low quantity of oil binder (as seen in backscattered images of the affected areas leading to the brittleness in the paint and its consequent lack of adhesion between layers.

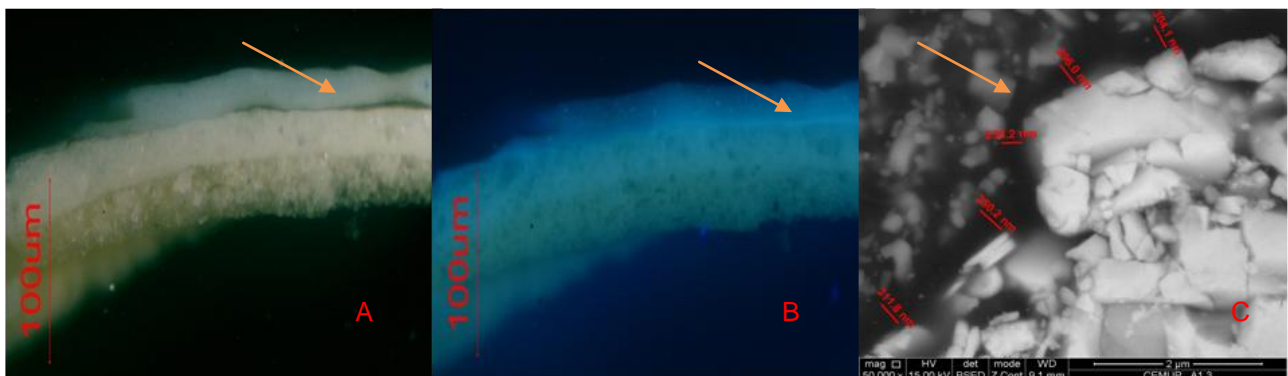


Fig.35: Cross-section A1.4. A: OM 20x, visible, reflected polarized light.; B: 20x UV light. C: Backscattered image of cross-section detail of distance between *imprimatura* and painting layer. The arrow indicates the thin layer in between both layers.

What may be binder migration to the layer's interface encouraging separation can be observed in fig. 35 above. In this cross-section it's possible to observe, with visible polarised light, the presence of a very thin translucent layer, which under UV light, gets a milky aspect (fig. 35 B). A SEM-backscatter image (fig. 35 C) indicates an average measured distance of approx. 300 nm. This translucent layer may represent the migration of binder, or zinc soap formed due to the reaction of the binder with the Zinc Oxide pigment.

The paint instability and risk of further flaking due to interlaminar cleavage, made it necessary to do an *urgent* consolidation treatment in these areas first. Before application of the adhesive it was necessary to soften the brittle paint layers. For this reason, a local humidification system was used: a bridge of moistened blotter paper on top of the area needing to be softened (Fig.36). This was covered by polyester film (Melinex) to preserve high humidity for a short period.

To adhere delaminated paint, *Lascaux Medium for consolidation*[®] (Kremer pigments) was used in stock solution. This is an acrylic copolymer, water based, synthetic adhesive (μ -FTIR analyses were done to check the formulation). The adhesive was applied with a soft brush *Pro Art* No. 1 (England, 100 series). The excess adhesive was removed with a small cotton swab moistened with water. Consolidated areas were then lightly heated with a hot spatula. Silicone coated Melinex[®] was used on the paint surface during the application of heat left in place while sand weight was applied during cooling. The paint surface was gently brushed with a soft brush to remove dust before testing colour areas with a surface cleaning solution (distilled water and the surfactant Surfynol 61[®] (from Kremer Pigments) in a dilution of 0,66% in water [35]). Once established as safe, the paint surface was gently cleaned of surface dirt using this solution. Surfynol 61[®] was chosen as it is volatile; therefore it is evaporated entirely off the surface without leaving any residue. The cleaning was done with slightly moist cotton swabs in circular movements in areas of about 4 cm² (see fig.64; Ap. XVII)

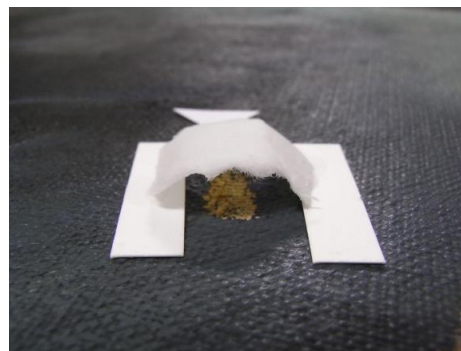


Fig.36: Local humidification treatment system used to soften the brittle areas with detachment problems.

5.1 TREATMENT TO REMOVE OUT OF PLANE DISTORTIONS

Moisture treatments are a frequent method for flattening textile supports. They can be used to improve the flexibility of textiles and to eliminate (or reduce) planar distortion in a painting [16]. Water acts as a plasticizer as the small water molecules penetrate onto the amorphous regions of the cellulose, preventing close contact between the polymer chains and thereby increasing the free volume in these amorphous regions. As a result, the flexibility and softness of the textile increases [16]. Fibers reach an equilibrium moisture content with the moisture content of their environment. The aim of using moisture is to bring a fiber into a “visco-elastic state” [36]. In this state, the polymers (chain molecules) such as cellulose, can slide along each other and reorganize into their relaxed (i.e. energetically favorable) configuration [36] This explains why creases in textiles can be eliminated, or at least reduced, by humidification treatments. However, as noted in chapter III.3 (size layer), the speed of moisture take-up for each component in a painting (leading to a plastic state) is different, and the response to moisture (alteration in material properties) for each component also varies greatly. The fabric and the size layers can achieve a plastic state and respond very quickly to a rise in RH, whereas oil paint layers and an oil based ground require much higher RH for a longer period to become plastic. As Gerry Headley stated in “The practicalities of the interaction of moisture with oil paintings on canvas”, “the ground layers that comprise mixtures of lead white and calcium carbonate in an oil medium, “only reach plastic state with near saturation levels” [7].

The greatest danger in carrying out a moisture treatment, is that the high humidity needed to plasticise paint and ground can result in swelling the size layer, or canvas shrinkage, both of which can result in complete

delamination of the paint and ground from the canvas (the size can act as a release layer). Because size and canvas respond to high RH within seconds to minutes, whereas the oil paint/ground layers take much longer (up to 10 minutes), a system to control moisture exposure was needed. To accomplish a differential humidification or (humidification gradient) throughout the structure of the painting, the introduction of moisture to the system was primarily made from above, so the painting layers could be exposed to high levels of moisture and could therefore absorb it slowly without the canvas/size layer being immediately affected. Moisture exposure continued only to the point when deformations in the canvas/ground/paint composite felt relaxed (no longer stiff and resistant, but easily depressed with gentle hand pressure), then the source of moisture was quickly removed and the painting flattened while still in a plastic state. Experience with flattening the tacking margins indicated that the system would grow inflexible again within 60-120 seconds after the moisture source (moist blotter) was removed.

Another essential point, when performing the flattening treatment, was having the painting face up in all steps, since there was a danger that the moisture treatment could result in further paint layer delamination. If the painting was face down during this treatment, there was a risk that any delaminating paint would be lost, but by having it face up throughout, any loose paint would remain *in situ* and would be easily treated by consolidation. Because of its size a team was needed to handle the painting, and since moisture response would happen quickly, all aspects of the method, procedure and materials used, had to be well planned in advance. Therefore every step was previously tested and rehearsed.

5.1.1 THE HUMIDITY CHAMBER

For controlling the introduction of moisture, a humidification chamber was designed, built and tested. A rigid metal screen of 1,80x1,80 m was suspended over a table using plastic boxes for support around the edges. Four blotters (dimensions: 0,86x0,61 and 2mm thickness) were each sprayed to saturation with distilled water and left to equilibrate while wrapped in polyester film (Melinex®). A large piece of polyester film (Melinex® joined with tape) was used to cover the metal screen and supports such that the area under the screen where the painting would be, was airtight. A data-logger was placed in the centre under the screen, and the four wet blotters introduced. The time taken to achieve a maximum of 85% RH was recorded (15 min). When it became evident that 4 blotters would result in RH levels above 85%, one blotter was removed, and the chamber monitored to establish that a constant RH level of 85% could be achieved. It was also established that the RH could be immediately lowered by opening the ends of the chamber and blowing fresh air in with a fan. The weight of the wet blotters were recorded, then they were allowed to dry to ambient conditions and weighed again to determine the weight of water they carried when the chamber was maintained at 85% RH. By this means it was established that each blotter should have a total of 100 grams water added in order to deliver the appropriate moisture to the space at ambient temperature (24°). On the day of the moisture treatment, four blotters had been prepared 24 hours beforehand and kept wrapped in Melinex®. Because of the moisture lost to the painting, the fourth blotter was needed to achieve 85% RH within the chamber.

5.1.2 SUMMARY OF PREPARING FOR THE MOISTURE TREATMENT

Because it was necessary to keep the painting face up during moisture treatment followed by the use of heavy weights to flatten, it was imperative to create a seamless perfectly flat surface directly underneath the painting, which would fully support the paint/ground/canvas composite throughout treatment. Since the

paint/ground would be in a plastic state, any distortions (seams, undulations) could be transferred to the painting and become fixed in its surface (normally paintings can be placed face down on a perfectly smooth surface, which provides the necessary support). Furthermore, to effect the treatment face up, it would be necessary to turn the painting over after it had been detached from its stretcher (detachment was necessarily carried out face down). Therefore a means to both support the painting during treatment and create a sandwich to allow it to be safely turned over was designed as part of the treatment process. Because of its size, a team of 6 to 7 people were needed to handle the parts of the support system, and to turn the painting and place it in the humidity chamber. The team was also necessary during an initial moisture treatment of the canvas to ensure even exposure to moisture in a highly controlled manner.

5.1.3 THE TREATMENT, STEP BY STEP

PART 1 (Top portion of the sandwich, straightening the back of the tacking margins and dust removal)

Step 1

A. The painting was placed face down on top of a sheet of thin Melinex® (polyester film). Below this was a single sheet of cushioning material⁶ which sat on top of a single sheet of Coroplast® (polyethylene board). These materials were all on top of a perfectly flat, seamless table top. The sheet of Coroplast® would eventually be the top surface of the sandwich. The cushioning material was present to prevent the flattening of the *impasto* while the painting, in a plastic state, would be put under pressure. The sheet of cushioning material was cut larger than the painting surface so that it could be wrapped around to protect the tacking margins within the sandwich (see fig. 38).

B. To allow the sandwich to be held together in a unit when complete, 22 long pieces of adhesive tape 40 cm were prepared as straps such that the ends were left exposed (with their adhesive) and the central portion was covered with Melinex®. The straps were applied at regular intervals around the Coroplast sheet, adhered to the underside of the Coroplast® with the strip and the other adhesive end left free (fig.37). Eventually these straps would hold the top and bottom of the sandwich together (see below).

C. For the safe removal of the stretcher in order to build the sandwich and to allow the painting and canvas to move while returning to plane during and after the moisture treatment, it was necessary to remove the tacks along all tacking margins, and to straighten the tacking margins (see fig 88, Ap. XVII). For this reason, a localized moisture treatment was performed on each of the tacking margins where excess canvas was turned over due to the back of the stretcher. Blotter papers were cut to size in strips, and were very lightly moistened and placed against the canvas until the canvas/ground became flexible enough to be straightened. Long pieces of wood were placed against the flexible tacking margins with lead weights to secure them in place such that the tacking margins were held straight until they “set” in their new position (see fig 66 Ap. XVII) (once the moist blotters were removed the canvas/ground lost flexibility within 30-60 seconds, but required time with weights to take on the new position).



Fig.37: placing the stretcher bar on the canvas back

⁶ The cushioning material is a very soft cloth with thin layer of plastic on one side, used for paper treatment and wasn't identified.

D. After the back of the tacking margins were straightened, the stretcher was removed, and the back of the painting was mechanically cleaned with a soft brush (the nozzle from a vacuum cleaner was held above to collect dust and debris dislodged by the brush).

PART 2: building and assembling sandwich components (Units A & B)

Unit A Assembly

Step 1 (protecting the canvas and providing a seamless layer directly under the canvas)

1.A a thin (12µm thickness) piece of Melinex® was cut to the size of the back of the painting (not including the tacking margins) and was laid on top of the canvas.

1.B A seamless piece of heavy white paper⁷ the exact dimensions of the inside edge of the painting was placed on top of the Melinex®.

Step 2

2.A A single sheet of medium weight card board was assembled from separate pieces attached with tape on the underside. Sheets were placed edge-to-edge (butt edged) to form a single smooth sheet. The corners and edges of the top surface were sanded to remove any sharp edges where the cardboard might contact the canvas.

2.B 16 long pieces of adhesive tape (30 cm) were prepared as in Part 1. The tapes were attached to the underside of the cardboard at regular intervals around the edge. The excess was left hanging out, as the other ends of the tape would be wrapped around the stretcher and secured to K-line inserts(see below), such that the cardboard/stretcher/K-line inserts made a complete independent unit that could be lifted off the painting in one piece (Unit A) (see fig. 69; Ap. XVII).

2.C Because the underside of the stretcher was not flat, extra cardboard was cut to the size of the stretcher bars to create an even surface over the underside of the stretcher prior to the stretcher being placed within the Unit A assembly (see fig 70; Ap. XVII).

2.D To create an even surface at the back of the stretcher, the four central sections of the stretcher, were filled with squares of multiple layers of foam-core stiff board (K-line) held together with adhesive. These were the same depth as the stretcher (see fig 71 Ap. XVII).

2.E Adhesive tapes were brought around from the cardboard sheet (Step 2 B) and affixed to the K-line inserts, thus creating a single assembly (Unit A) (see fig 72 Ap. XVII).

(Unit B assembly)

STEP 3

3.A To form Unit B, 5 layers of Kapa-line sheets (foam core with plasticised paper surfaces) were cut to the size of the stretcher (single sheets were butt edged and seams were off-set from each other in the following layers to reduce the impact of seams). The layers of K-line were held together with adhesive tape around the edges, thus creating a smooth and even single platform that was then placed on top of Unit A. The thickness of Unit B was such that it was thicker than the total length of the extended tacking margins [so that when the entire assembly was upright in the humidity chamber, the tacking margins would hang down freely without touching the table (fig 45, below).

⁷ From the photography studio, this paper comes on a roll and is used for background in photography. It is wide and seamless.

STEP 4 (assembling the sandwich to allow the painting to be turned over)

A. When the sandwich was being assembled, the adhesive tapes which had been adhered to the Coroplast® (Part 1, Step 1 B) were then brought around and adhered to the top of Unit B, thus creating a secure lightweight sandwich (see fig 73; Ap. XVII)

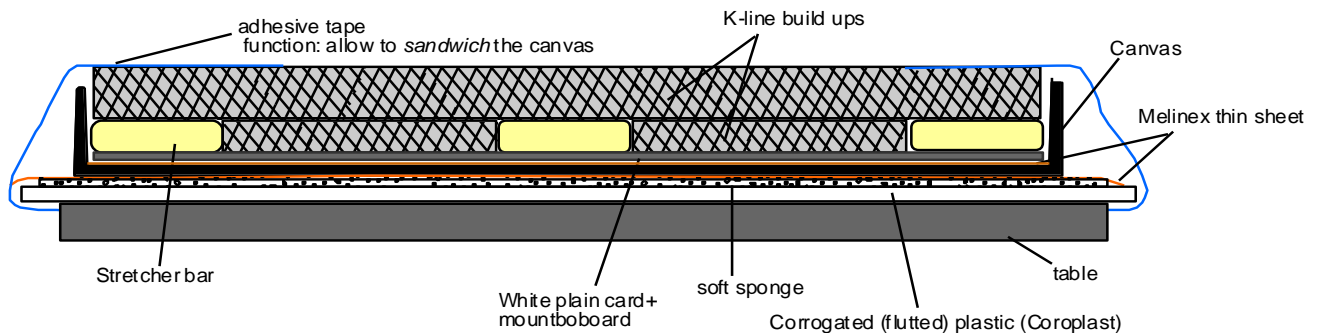


Fig.38: Cross-sectional view of method used for flattening Sinfonia Heroica's painting: way to turn it upside without being attached to the stretcher.

PART 3. (The moisture treatment sequence)

3.A Tests of moisture treatment of the paint layers alone indicated very slow response to moisture. Because of the success using moist blotters in direct contact with the canvas while flattening the tacking margins, to effect a better relaxation of the canvas, it was decided to expose the back of the canvas very briefly to barely moistened blotters prior to the full moisture treatment of the paint in the humidity chamber. Blotters were cut to fit the back of the painting. Each blotter was numbered in pencil and a map of where each blotter fit on the back was drawn. All 7 members of the team were assigned specific blotters, such that the application of the blotters could happen at the same time so that the canvas was exposed evenly at once to the moisture. The blotters had been very lightly sprayed with distilled water and left wrapped in Melinex® to equilibrate prior to use. The blotters remained in contact with the canvas for a short period (3-4 minutes) with a layer of Melinex® placed over top to keep the moisture exposure uniform. When the canvas/ground/paint composite felt flexible, the blotters were quickly removed by the team and the thin sheet of Melinex® left covering the back of the canvas to maintain moisture while the sandwich was being constructed.

3.B The sandwich units were assembled and held together with adhesive straps (Fig.39), then the team turned the sandwich upside down so that the painting was oriented face side up (see fig. 73; Ap. XVII).

3.C The adhesive tapes, the Coroplast sheet, the cushioning cloth and the Melinex® sheet were removed, and the painting with the lower portion of the support assemble (Units A & B) was moved to the humidity chamber (previously assembled on another table).

3.D After the painting was placed inside the chamber, the moist blotters were laid on the screen and the Melinex® cover secured. The relative humidity within the chamber gradually increased to 85% RH (25°C). The RH was maintained at this level [16] for approximately 11.5 minutes (the time it took for the deformations to gain flexibility (relax) which was determined by touch (see fig. 74 and 75; Ap. XVII).

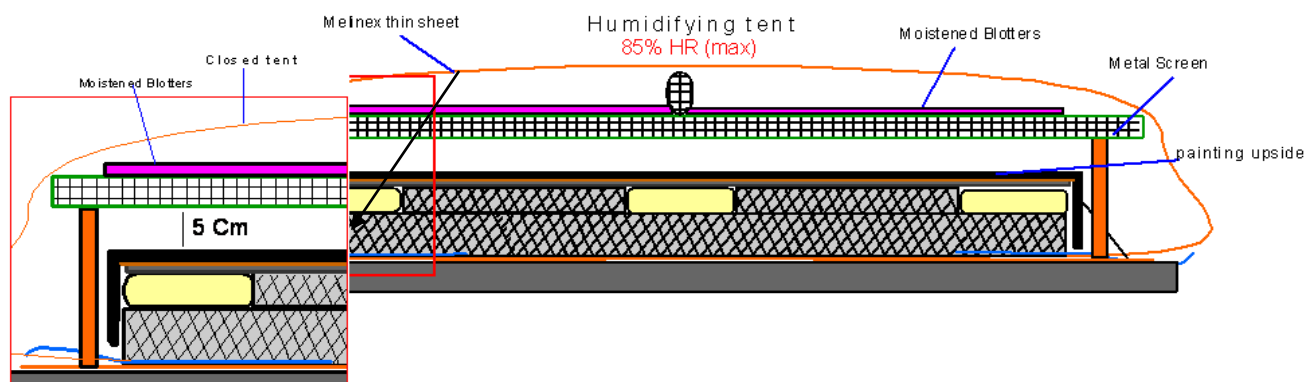


Fig. 39: Cross-section scheme of humidity chamber.

3.E After that time, the moist blotters were removed, and with the sheet of Melinex® covering the humidity chamber still in place, a thin sheet of Melinex was placed on top of the painting followed by the cushioning material. At this point the Melinex® covering the chamber was removed, the metal screen taken off, and the painting quickly moved, face up, to the first table. The Coroplast sheet was again placed on top of the painting (which was protected by the cushioning cloth and the layer of Melinex® immediately against the paint), and a series of heavy wood-fibre boards were placed on top to provide pressure to effect flattening while the paint/ground/canvas composite was in a plastic state. Further pressure was supplied by more fibre boards with lead weights on top (see fig. 78, 79, 80 and 81; Ap. XVII).

3.F During the first day the painting was checked 2 different times, to make sure the paint layers were reacting as desired. It stayed under pressure for 61 hours and after was checked with raking light. Overall the painting appeared quite flattened except at the top edge where a localized flattening treatment was deemed necessary to even-out some small deformations.

PART 4 (stretcher adjustment and re-attachment of the painting)

4.A The weights were removed and the sandwich reassembled so that the painting could again be turned face down (a team of 6 were needed).

4.B With the painting face down, all support materials were removed. When the stretcher was reattached to the back of the painting it was observed that the turn over edges of the painting remained close to the edge of the stretcher (the painting had not expanded during treatment) so the stretcher could be used without further modification other than keying-out [37].

4.C Because there were no original keys in the stretcher, 11 pine keys were customized by sanding to reduce their thickness and were put in place. The stretcher was keyed out slightly prior to the painting being re-adhered to the stretcher (for procedure see CCI note n°10/9 “Keying out paintings” [38].

4.D After consulting the study made by Cristina Young and Robert Hibberd “The Role of Canvas Attachments in the Strain Distribution and Degradation of Easel Paintings” [39] it was decided that the best system for the painting was to place a series of tacks regularly spaced, but with much smaller spaces between than had been originally used (tacks were placed at intervals of 4 cm). Strips of acid-free card were placed between the canvas and the tacks as the taking margins were being secured. To create enough

stiffness, two thin sheets of the card were cut in strips and adhered together with double-sided archival tape. The acid-free card was present to protect the canvas from being in touch with the potentially corrosive steel tacks and to supply a degree of pressure along the edges to reduce the return of undulations in the fabric/ground between the tacks. 150 Standlers® black steel tacks (11 mm long) and 10-12 tacks 9 mm long (from) were used. While the tacking margins were re-adhered, the painting was held flat with the K-line inserts between the stretcher sections (see fig. 82 and 83; Ap. XVII).

4.E To complete the treatment, the excess tacking margins which had been straightened at the outset of treatment, were repositioned at the back of the stretcher with local moisture treatments (as described in Part 1, Step.1 C) followed by flattening.

Conclusions

Overall the study and treatment of the painting *Sinfonia Heroica* demonstrated that large paintings require specific handling, materials, facilities and technical support that are a challenge to manage.

In terms of accomplishing the treatment the conservation problems regarding the interlaminar cleavage and detachment could be immediately solved through consolidation treatment, but the cause is still unclear and can be due to several issues:

1. Micro-sampling of the composite layers in areas that presented interlaminar cleavage and detachment was not possible without the layers immediately separating, making it impossible to have an intact sample. The fact that all cross-sections from area A1 (the main interlaminar cleavage area) were from the separated paint layers (the bottom one attached to the ground and the top one alone) could lead to a misunderstanding or loss of information: if there was a formation of zinc soaps that had migrated to the interlaminar space, because of their soft and perhaps very thin nature, this evidence could be lost in the process of resin embedding for cross-section. The sample photographed with SEM-EDX, showed a substance in-between the paint layers with a translucent with viscous appearance whose origin and composition is still not determined. Further analyses would be needed using (FTIR imaging for example)
2. The role of zinc is still undetermined. The fact that almost every sample taken showed the presence of zinc could derive from zinc oxide pigment added to lighten the colour of the paint or from a previous addition to the paint by the manufacturer (e.g. zinc stearate). The zinc containing paint showed a high pigment density. Perhaps through compressive forces, or incompatibility with other materials, zinc soaps or binder components migrated out, resulting in brittle paint layers. There are reports in the literature, that zinc white pigment causes brittle paint, although the mechanism for this was not explained.
3. The identification of bloom was not possible because it was impossible to acquire a sample: it is composed of a very thin layer and its visibility/presence varied with changes in relative humidity. Under low relative humidity it is more visible but when the RH rises it becomes less visible, possibly meaning its structure hydrates and de-hydrates forming a transparent or whitish colour on the surface respectively, or that it is part of the paint layers or varnish which re-dissolves and is transported to the interior of the layer. The overall flattening treatment was a success, with a restoration to plane for over 90% of the surface. In some areas however, local flattening treatment will be needed to return small areas to plane.

Because of the paintings history of distortions and its RH susceptibility, it will be necessary to maintain constant and appropriate RH and Temperature values. Fortunately this is already being provided by the Culturgest facilities where the painting will be stored after treatment.

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APPENDIX I: LETTER SENT BY ARCHITECT DORDIO GOMES

The Document above, is the letter sent by Architect Dordio Gomes, son of the painter Dordio Gomes, in response to a previous e-mail with questions about the artist, his material and techniques.

The letter was sent through his grandson, André Dordio Gomes on 23 of April 2010.

2.1/ TÉCNICAS DE TRABALHO

1. — NÃO SEI SE TERIA ALGUMA TÉCNICA ESPECÍFICA.

2. — SEI QUE GANHAVA DE PINTAR SOBRE TELA JÁ PINTADA APROVEITANDO VÁRIAS MANEIRAS E ALGUNS ELEMENTOS EXISTENTES NELA A-FIM DE FICARME NA JORNADA COMPOSIÇÃO VISUAL.

3. — A ÚNICA TÉCNICA QUE ME LEMBRO, COMO SER UMA TÉCNICA CLÁSSICA:

— COMEÇAR POR DEFEINIR A COMPOSIÇÃO, AS CONTRAÇÕES DAS ELEMENTOS, COM A PRÓPRIA TINTA O ÓLEO, MISTURADA COM O AÍCIO DE LINHAGA USANDO O PINTEL.

— AO DEFEINIR OS ELEMENTOS, SE SEMINANDO COM O POUQUÍSSIMO PARA DEPOIS EM SEGUIR PREENCHER OS ESPAÇOS EM TINTA, PREFERINDO O MUITOS VEZES ALTERNANDO A COMPOSIÇÃO ATÉ AO FINAL DA OBRA. ACABANDO.

- A MUITAS VEZES INCOMPLETA, ISTO É — INACABADA

2.1/ MATERIAIS

— MATERIAS — CREIO QUE NÃO TINHA —

— CREIO, ISSO SIM — UM MISTO — NA REALIZAÇÃO DOS SEUS TRABALHOS: ÓLEO, —

1. — POTS DE OS CORTEZ, ESTIVIZAVA OS COM SEGUROS / ESTADOS AO INVESTIGAVA O (O) PER-SONAGEM (OS) NA CENA QUEIA REPRESENTAR NOS SEUS TELAS (AVANÇOS) OU NAS PARQUES (FOTOGOS).

2. — QUANDO TRABALHAVA A TELA SABIA DE ANTEREÃO O QUE IA FAZER. E POR ISSO QUE SE ADOCEAVA DE DESEJO / ESTADOS, INCLUSIVE FEITOS, E DE LIVROS / REPRODUÇÕES AO LENDO.

— UM FACTOR SEMPRE O PRECUPAR — A COMPOSIÇÃO

3. — TODA A SUA PINTURA É UMA PINTURA LINGUÁVIA NITIDA DA SUA FORMAÇÃO ACADÉMICA (1904/1909, GOLBO QUE PREZEMOS DIZER, EM ADOBO DA VERDADE, — UM ACADÉMICO NO BOM SENTIDO DA PALAVRA —

2.1/ MATERIAIS

PINCEIS / TUBOS DE TINTA / PAQUETA DOS DE CADAÚO / ÓLEO DE LINHAGA

1000

PIRELLA GOM A MARCA - WINDSOR E MONTANA
MADE IN ENGLAND

Figure 1. The study area.

1000

[illegible]

Q1. Why?

1

3.4 SENS. ADJUSTMENTS

[illegible][illegible]

$\Gamma \in \Pi_{\text{reg}}^{\text{reg}}$ and $\Gamma' \in \Pi_{\text{reg}}^{\text{reg}}$ are adjacent if and only if

$$-1 \leq \frac{v_1}{v_2} \leq 1 \quad \text{if} \quad \frac{v_1}{v_2} \leq \frac{v_3}{v_4} \leq \frac{v_5}{v_6}.$$

3.4/ PESSOAS MAIS PRÓXIMAS

1003f — 2M 2,010 — PBRFC - 1st Division LA

[illegible]

Juliao da Rocha - Fundação João Cabral de Oliveira

L0610, SER 4038, A WATCIN PC5500A LIAAS VACUUM CH

— Sur le p^resentement d'acte, voir l'écrou p. 2. —

[illegible]

СЛУЖБЕ РЕГИСТРАЦИЈЕ И ЗАПИСИ

[illegible]

LAURENCE JULIO POLORE.

$$A_2 \cup B_2 \cup C_2 \cup D_2 \cup E_2 \cup F_2 \cup G_2 \cup H_2 \cup I_2 \cup J_2 \cup K_2 \cup L_2 \cup M_2 \cup N_2 \cup O_2 \cup P_2 \cup Q_2 \cup R_2 \cup S_2 \cup T_2 \cup U_2 \cup V_2 \cup W_2 \cup X_2 \cup Y_2 \cup Z_2$$

_____JU 10 0 0 6 @ CENTRE FOR B&M

3.5 / ENCOMENDA

1. - A REALIZAÇÃO DA PINTURA EM ESTUDO - O QUE NÃO FOI ESCOLHIDO PELO ARTISTA, MAS, SIM, PELA PESSOA QUE O ENCOMENDOU.
2. - TRATAVA-SE DE UM GRANDE AMIGO DA NOSSA FAMÍLIA UM GRANDE INVENTOR DO ALENTEJO, COM A SUA HABITUAÇÃO EM ÉVORA - ENGENHEIRO AGRÔNOMO - TENDO IDO À SUÍÇA ONDE ESTUDOU E ONDE CONHECEU UMA SENHORA COM QUEM CASOU, TENDO 3 FILHOS.
- GRANDE AMANTE DA MÚSICA, A SUA MULHER ABROGAVA-O NESTE GOSTO, POIS TOCAVA PIANO E MUITAS VEZES, POR NÃO DIZER NUNCA, UM DOS SEUS FILHOS, ACOMPANHAVA-A AO VIOLINO
- A MÚSICA FAZIA PARTE DA SUA VIDA
3. NA SUA CASA EM ÉVORA, NA SALA DE ESTAR, VERDEIRO SALÃO, EXISTIA UMA GRANDE PAREDE EM QUE ERA OCUPADA POR UM MÓVEL CUBRIDO - CHEIO DE DISCOS - ESTANDO POR CIMA DESTA A PINTURA EM ESTUDO;
- SINFONIA HERÓICA / BEETHOVEN

POSSO ALRESCENTAR QUE FOI NESTE SALÃO QUE MEU PAI OUVIU AS NOVE SINFONIAS ANTES DE COMEÇAR O SEU TRABALHO EM CAUSA.

- ESTÁ AQUI MAIS UMA PROVA QUE O ARTISTA ANTES DE COMEÇAR A OBRA - INVESTIGAVA / ESTUDAVA - IMPLANTAVA-SE NO TEMA DA OBRA QUE IA REALIZAR.

5. / COMPLETAMENTO

1. - JÁ FOI DITO QUE MEU PAI ANTES DA REALIZAÇÃO DE QUALQUER OBRA GOSTAVA DE FAZER DESENHOS / ESTUDOS.
PORTANTO, É MUITO PROVÁVEL QUE EXISTAM TRABALHOS QUEER A ÓLEO, DESENHOS, A CARVÃO.
2. - A FOTOGRAFIA, EM QUESTÃO, É UM DESES ESTUDOS QUE REALIZOU, VISTO QUE O SENHOR POSSUIA UMA RÉPLICA, TANTO BASTO PEQUENO, DO TRABALHO EM ESTUDO - BEETHOVEN -


12/08/2010



Fig. 1: Dordio Gomes study for Sinfonia Heroica/ Beethoven. Oil (?) on plywood, 32x40 cm. Photograph by Diana Conde.



Fig. 2: Painting "Auto-Retrato da Natureza Morta". by Dordio Gomes, 1925, 1,50x90 cm. Closer observation to this painting indicated the interlaminar cleavage similarities. Photograph by Diana Conde.



Fig. 3: Dordio Gomes painting pallet. Photograph by Diana Conde.



Fig. 4: Dordio Gomes painting brushes. Photograph by Diana Conde



Fig. 5: Dordio's Gomes Winsor and Newton paint tubes: Ivory black, Yellow Ochre, Venetian Red, Ultramarine deep, Naples Yellow, Viridian SL, Ivory black, Rose Madder genuine and Lefranc's Rouge de Cadmium. The red dot marks the paint tubes analyzed with μ -FTIR.



Fig. 6: Dordio Gomes Rembrandt paint tubes: Flake white, Raw Sienna, Cadmium yellow lemon, Naples Yellow Imitation, Permanent Green Light, Prussian Blue, Cobalt Blue Light. Based on the layout of the labels and the shape of the cap design, the Rembrandt tubes have been dated from 1950-1955, by Stefanie Litjens, (a master student, University of Amsterdam Conservation Program, who is working on Dutch paint tubes from 1920-60). The red dot marks the paint tubes analyzed with μ -FTIR.

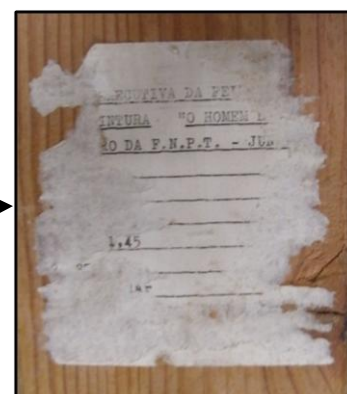


Fig. 8: Paper label adhered to the back of the stretcher, on the vertical cross bar.

Fig. 7: Photography of *Sinfonia Heroica*'s reverse.



Fig. 9: several Inscriptions on the stretcher bars regarding how they fit.

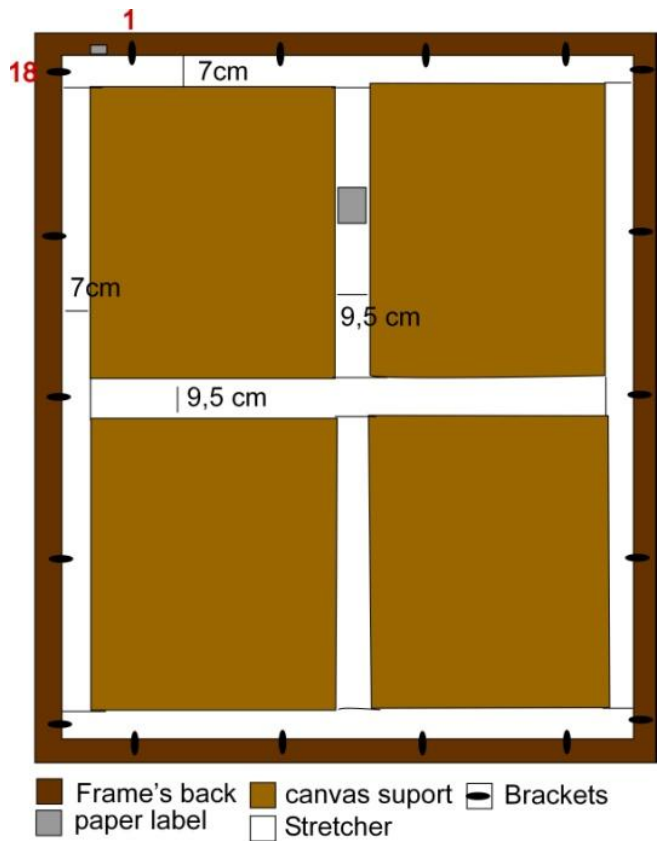


Fig. 11: Tacks and cardboard used to attach the canvas to the stretcher.

Fig. 10: Scheme of paintings reverse before treatment showing the stretcher bar measurements, number and place of the brackets holding the frame.



Fig. 12: Canvas support detail.

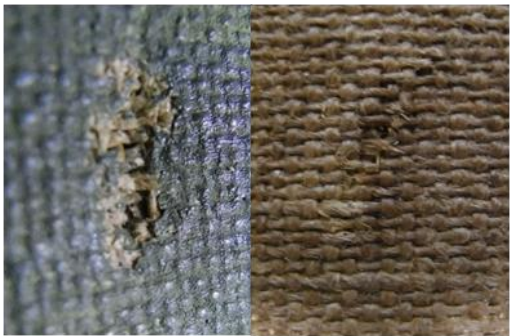


Fig. 13: Front and back view of tear detail of tear, situated on the 7th section (see Appendix IV: Examination Mapping).

APPENDIX IV: EXAMINATION MAPPING

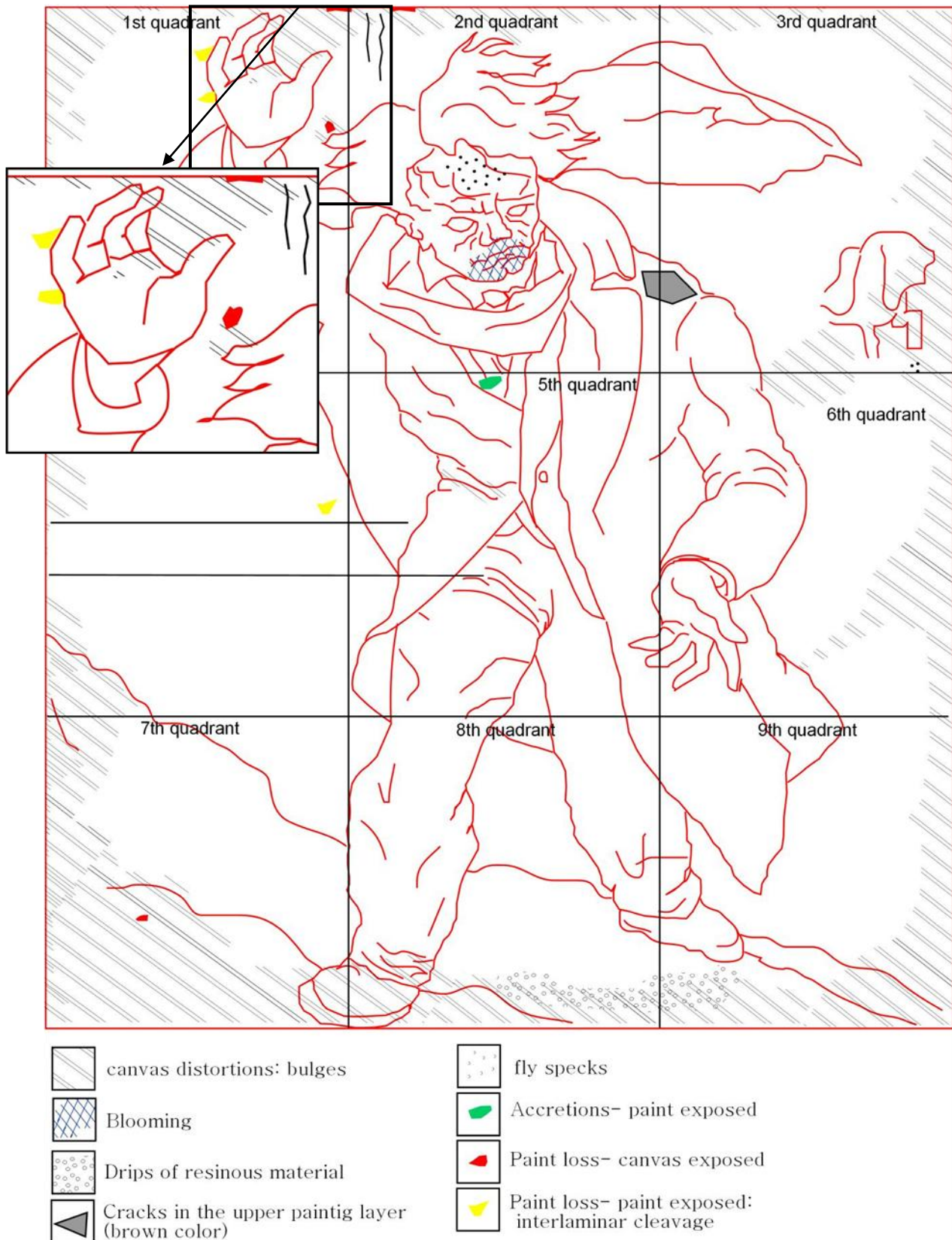


Fig. 14: Mapping of *Sinfonia Heroica*'s condition state.

**APPENDIX V: SINFONIA HEROICA'S EXAMINATION PICTURES: RAKING,
TRANSMITTED AND UV LIGHT PHOTOGRAPH'S**



Fig. 15: Picture with raking light.



Fig. 16: Back of the painting with raking light. The black arrow indicates the textile deformation and tear caused by mechanical impact.

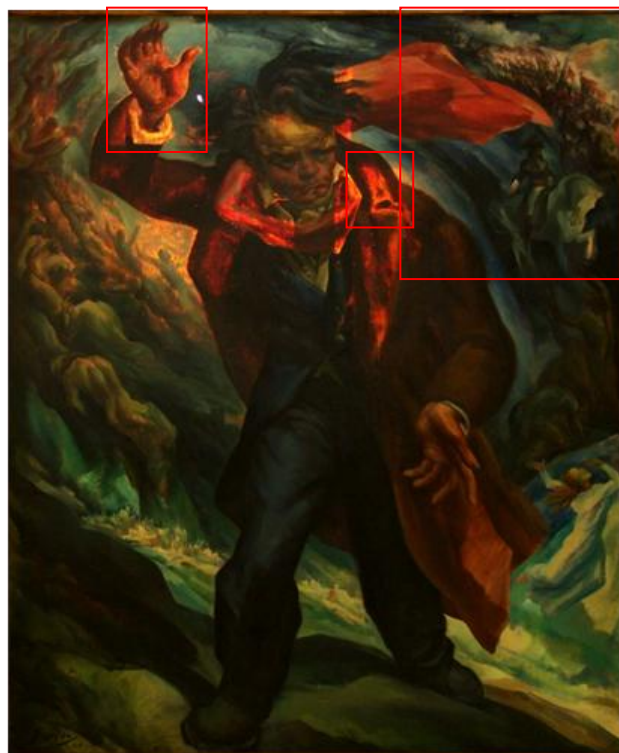


Fig. 17: Transmitted light photograph of Sinfonia Heroica.



Fig. 18: Detail with raking light: undulation on the left side according to the tacks position on the margins

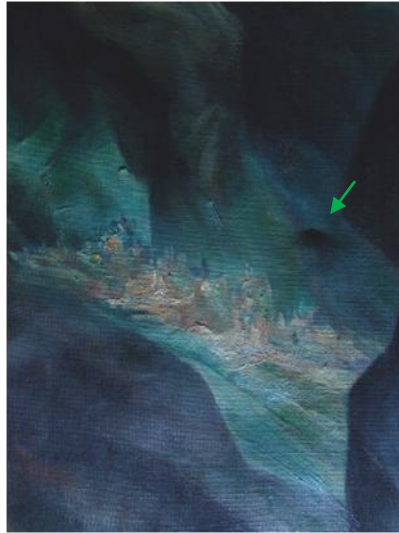


Fig. 19: detail with raking light: bulge probably due to impact



Fig. 20: detail with raking light: deformation that follows the colour area.



Fig. 21: Detail of surface abrasion/delamination of top painting layers under UV light (arrow).



Fig. 22: Detail of *Sinfonia Heroica* under UV light: Green fluorescence due to the surface coating and whitish fluorescence due to grey painting layer (arrow)



Fig. 23: Detail in U.V. light of right side of the painting showing no varnish at the edge where the frame covered the painting.



Fig. 24: Varnish brushstrokes and uneven fluorescence in U.V.

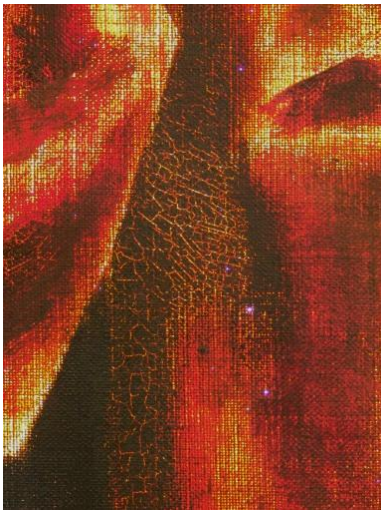


Fig. 25: Detail with transmitted light: drying cracks.



Fig. 26: Detail of abrasion of the top layer.



Fig. 27: Detail of abrasion on the edge caused by the frame in the right corner.



Fig. 28: Detail of gold paint from the frame.

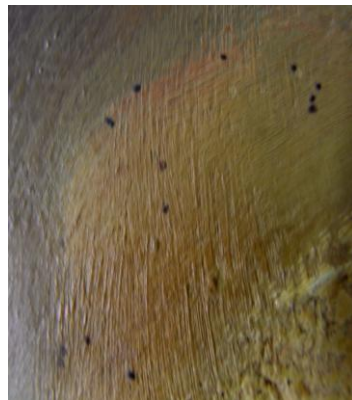


Fig. 29: Fly specks on the figures forehead, 2nd section.



Fig. 30: *Blooming* observed at the darker tones of the figures face.



Fig. 31: Infrared photography detail of bottom left corner showing possible pencil marks.

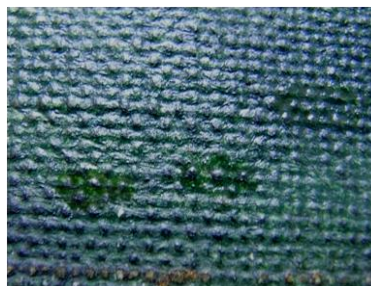


Fig. 32: Drips in the 8th section.



Fig. 33: photography of drips in the 8th section, under UV light.

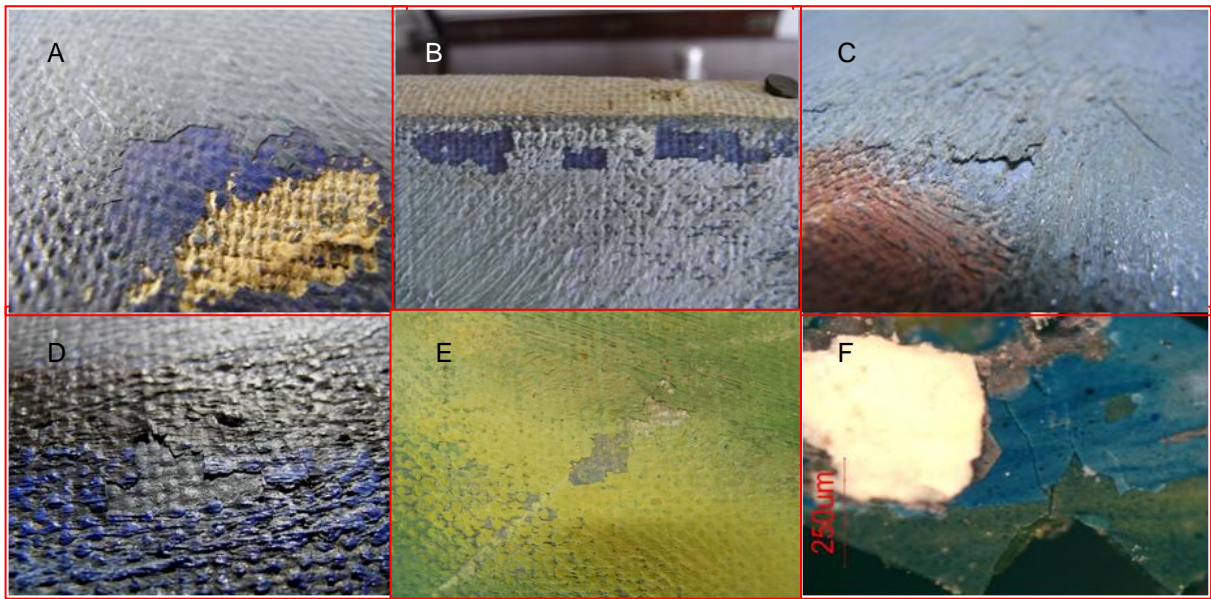


Fig. 34: Details of Sinfonia Heroica's interlaminar cleavage problems.

A: tear and lacunas with surroundings showing interlaminar cleavage in section 1. **B:** detachment of the top paint layers on the top of the painting section 2; **C** and **D:** detachment of the top paint layer, section 2; **E:** loss of the top paint layer possibly due to mechanical impact and abrasion; **F:** OM obs. from sample removed of interlaminar cleavage area, 250x visible light, dark field.

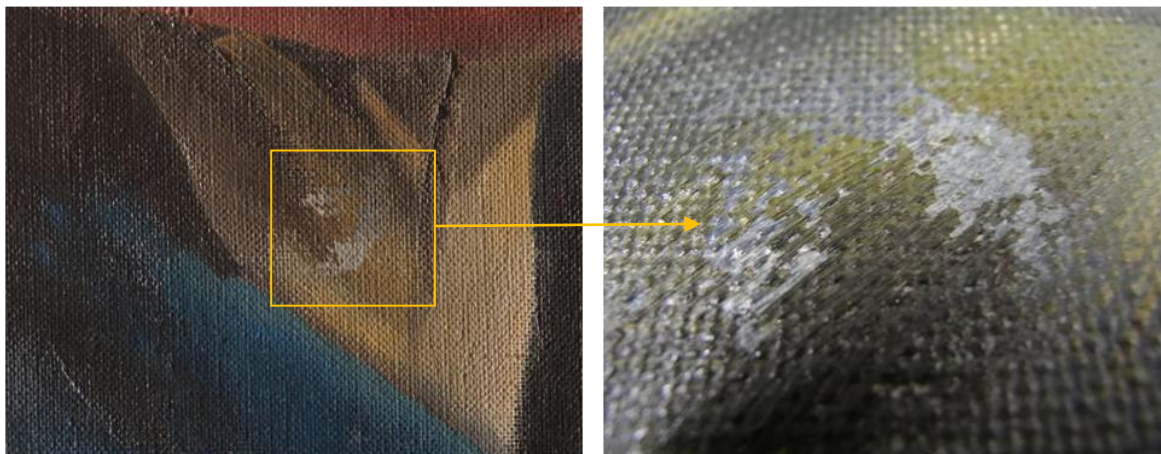


Fig. 35: Detail of surface abrasion situated nearby Beethoven's scarf.



Fig. 36: Sampling Areas

- Blue dots: cross-sections;
- Red dots: Micro-sampling for μ -FTIR and μ -Raman analyses;
- Yellow dots: ED-XRF analyses mapping.

APPENDIX X: INSTRUMENTS AND METHODS

To better understand how the painting was made 13 minute samples were taken from the edges of pre-existing losses or other areas of damage. These samples, were then mounted in cross-section and analyzed through X-Ray fluorescence as well as μ -Raman and, in some cases, SEM-EDX.

The main data acquisition for *Sinfonia Heroica* was performed on 24 March 2010 at the DCR painting laboratory. μ -EDXRF, analyses were done *in situ* while μ -FTIR, μ -Raman analyses were performed on micro-samples from the painting.

The strategy adopted to analyze colours began with the examination of cross-sections, then with μ -EDXRF analyses, followed by μ -Raman. The Micro-sampling to do μ -FTIR and μ -Raman were carried out under the microscope (Leica) using a micro chisel from Ted Pella micro tools.

Cross section methodology

All Cross-sections were mounted in a light curing embedding resin based on methacrylate (Technovit 2000 LC®) (38). Each Cross-section was hand polished with 7 successively finer grades of Micro-mesh abrasive clothes (300, 600, 800, 1200, 3600, 8000, 12000).

Optical Microscope (OM)

Optical analysis were carried out in an optical Zeiss Zxiopla Z Imaging microscope with a Nikon digital camera DMX 1200F and a mercury lamp HBO100.

Micro Fourier Transformed Infrared Spectroscopy μ -FTIR:

μ -FTIR analyses were performed on a Nicolet Nexus spectrophotometer interfaced with a Continuum microscope with MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, with spatial resolution of 50-100 μ m, an optical resolution of 4 cm^{-1} and 128 scans, by using a Thermo diamond anvil compression cell. The spectra are shown as acquired, without corrections or any further manipulations, except for the occasional removal of the CO_2 abs. at approx. 2300-2400 cm^{-1} .

μ -Raman:

The μ -Raman analysis were carried out using a Labram 300 Jobin Yvon spectrometer, equipped with a HeNe laser 17 mW operating at 632,8 nm. The selection of the excitation wavelength was chosen according to the colour of the samples, to optimize the results, avoiding fluorescence phenomena. The spectrum were obtained with 50X and 100X Olympus objective lens that result in a special resolution of respectively 4 and 2 μ m diameter. The potency in the samples was controlled through the application of a 0,1 mW (for laser 633 nm) and 3,75 for laser 532. The spectra were obtained in an interval of 50-2200. Using exposure times of 1-20 s and 3-15 accumulations. The laser beam was focused either with 50 x or 100x. The laser power at the surface of the samples was varied with the aid of neutral density filters (optical density 2).

Micro Energy Dispersive X-Ray Fluorescence (μ -EDXRF):

The equipment used to analyze the painting was an ArTax transportable spectrometer, Intax GmbH model, equipped with a X-ray Molybdenum (Mo) ampoule. The identification was made by exciting with a primary beam, with 0,3 mm diameter and a xFlash detector refrigerated with the Peltier (Sidrift) effect with a resolution below 170 eV. The analytic conditions were: 40kV of difference of potency, 600 μ A and 120 to 200 s acquiring.

Scanning Electron Microscopy Energy Dispersive X-ray Detection (SEM-EDX)

The SEM analysis was conducted in Centro de Materiais da Universidade do Porto (CEMUP), Porto with a FEI Quanta 400FEG ESEM / EDAX Genesis X4M, environmental scanning electron microscope with high resolution (Schottky) microanalysis, X-Ray Analysis and Electron Diffraction Pattern detector. The accelerator voltage of the system was 15 kV. The sample did not require coating. Appendix: HART Project Fiber Staining

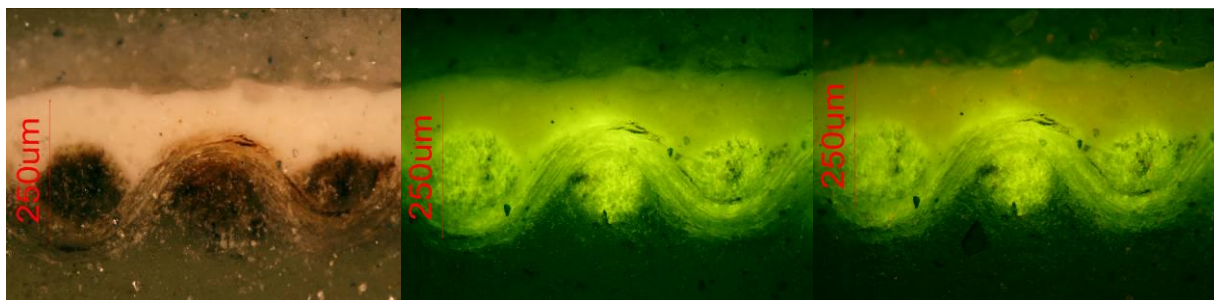


Fig. 37: Cross-section of Hart sample D2nCSO (no size layer application) under OM: 1- visible transmitted light, 250x; 2- UV light, Filter set 09: BP 450-490, FT 510, LP 515) before staining; 3- UV light, Filter set 06: BP 450-490, FT 510, LP 515) after staining.

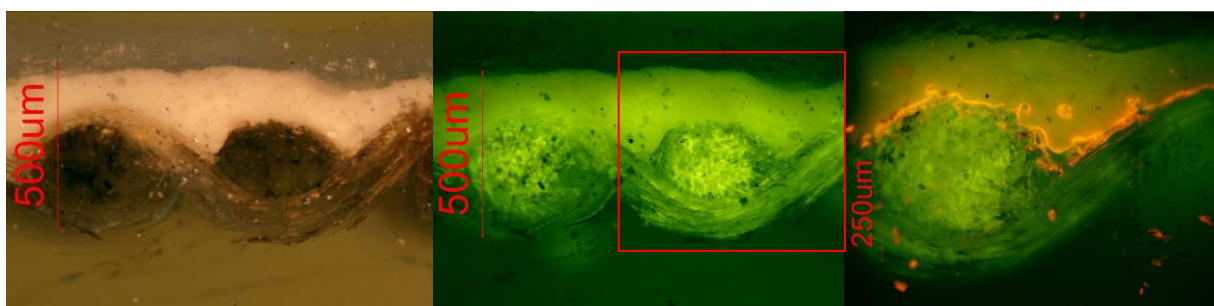


Fig. 38: Cross-section of Hart sample D2gCSO (Gel size application) under OM: 1- visible transmitted light, 250x; 2- UV light, Filter set 09: BP 450-490, FT 510, LP 515) before staining; 3- UV light, Filter set 06: BP 450-490, FT 510, LP 515) after staining.

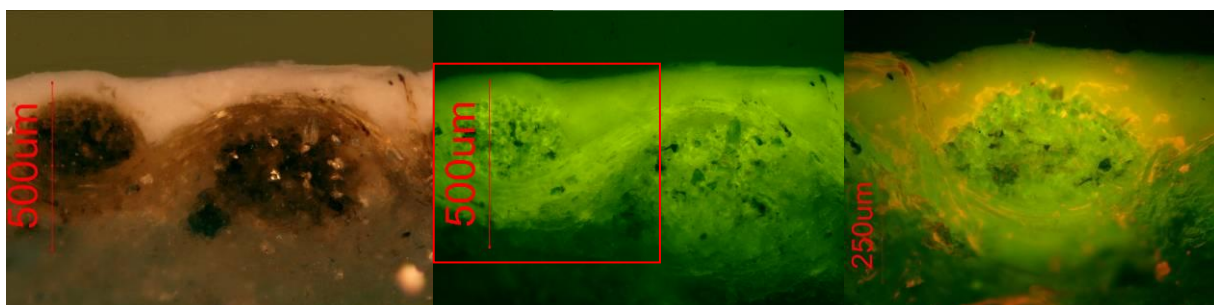
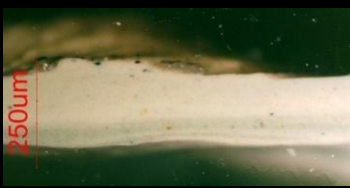

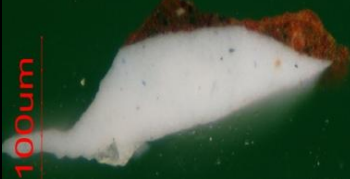


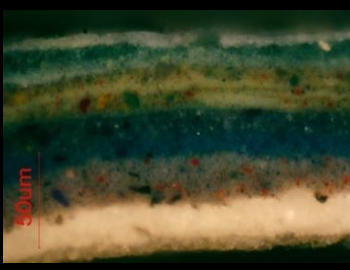
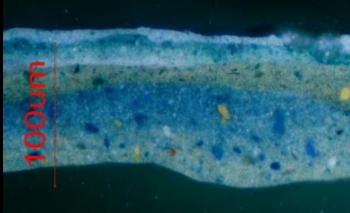


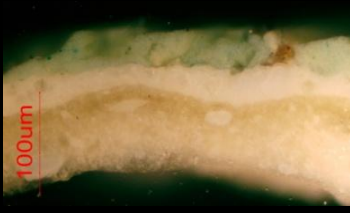





Fig. 39: Cross-section of Hart sample D2fCSO (fluid size application) under OM: 1- visible transmitted light, 250x; 2- UV light, Filter set 09: BP 450-490, FT 510, LP 515) before staining; 3- UV light, Filter set 06: BP 450-490, FT 510, LP 515) after staining.

APPENDIX XII: CROSS SECTIONS IDENTIFICATION AND ANALYSES RESULTS

Name	Area ID	Picture	SEM-EDX	μ-Raman Peaks	μ-XRF
A1.1	Top layer of interlaminar cleavage Colour: Greyish		area 1: C; O; Zn; Se; S; Cd	No sign	Fe; Zn
			area 2 (red dot): C; O; Zn; Se; S; Cd		
A1.2	Top layer of interlaminar cleavage Colour: Greyish		-	No sign	Zn
A1.3	Top layer of interlaminar cleavage near figure's hand Colour: brown		White dot, imprimatura layer: C; O; Pb	Brown Layer: Exc.wav.: 632,8 Mars Red (synthetic Iron (III))	Brown Layer: Zn; Fe; Cr
A1.4	Bottom layer of interlaminar cleavage Colour: light blue		area 1 (ground layer): C; O; Ca; Pb	Not identified Peaks: 1401; 1368 (exc. Wavelength: 632,8)	Zn; Co; Pb
			area 2 (dot in ground layer): C; O; Ca; Ti; Pb		
			area 3(white clast, Ground Layer): C; O; Ca; Pb		
			area 4: Layer pic: C, O, Zn		
A1.5	Top layer of interlaminar cleavage near figur's hand Colour: Brown		-	Brown Layer: Mars Red (synthetic Iron (III)) (Exc.wav.: 632,8)	Fe; Zn

Name	Area ID	Picture	SEM-EDX	μ-Raman Peaks	μ-XRF
	A2	Composite layers at edge of paint loss 	Area 1: Al; Si; Zn; S; Fe; Co; C; O	Grey layer: Lazurite (Ultramarine Blue)	Cr, Fe, Co, Zn, Pb
				Green Layer: Lazurite (Ultramarine Blue)	
			Area 2: C; O; Zn; S; Zn; K; Ca	Blue Layer: Lazurite (Ultramarine Blue)	
				Blue layer: Prussian blue	
				Red area: Mars red	
	A2.2	Top layers of top lacuna area Colour: Blue 	-	No signal	Cr; Fe; Co; Zn
	A3	Bottom Left lacuna Colour: Green 	-	Green Layer: No signal	Ca; Cr; Fe; Zn; Ba; Pb
	A4	Border central right Colour: Black/Dark Green 	-	Dark layer: Carbon Black	Ca; Cr; Fe; Zn; Pb
	A5	Border bottom right Colour: light Green 	-	No signal	Ca; Cr; Fe; Zn; Pb
	A6	Border top right Colour: Light blue 	-	No signal	Ca; Zn; Co; Pb
	A7	Border top right Colour: Light blue 	-	Yellow layer: Mars Yellow	Fe; Zn;
GL: Ground layers		Ground Layer: right side of tacking margin 	C; O; Pb; Ca	Upper Ground layer; Lead White (hydrocerussite)	Ca; Pb
			C; O; Pb; Ca; Si	Bottom Ground layer: Calcite CaCO ₃	

APPENDIX XIII: GROUND LAYER AND COLOUR ANALYSIS RESULTS

Table 1: Results of *Sinfonia Heroica*'s μ -XRF *In Situ* colour analysis. (For sample location, see Appendix VIII)

Table 2

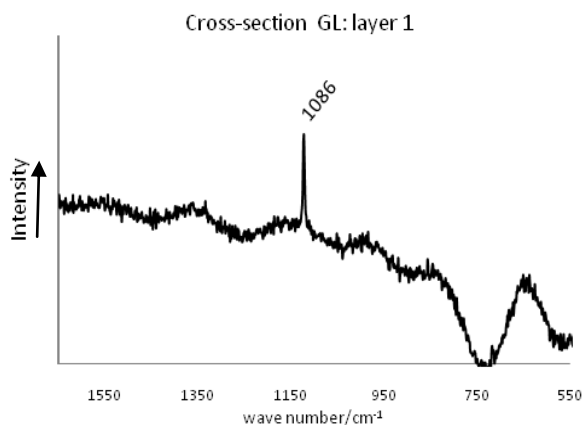


Fig. 40: μ -Raman Spectra of the ground layer (GL) cross-section, layer 1 ($\lambda=632,81$ nm), showing the strongest characteristic chalk CaCO_3 (calcite) peak at 1086 cm^{-1} (21).

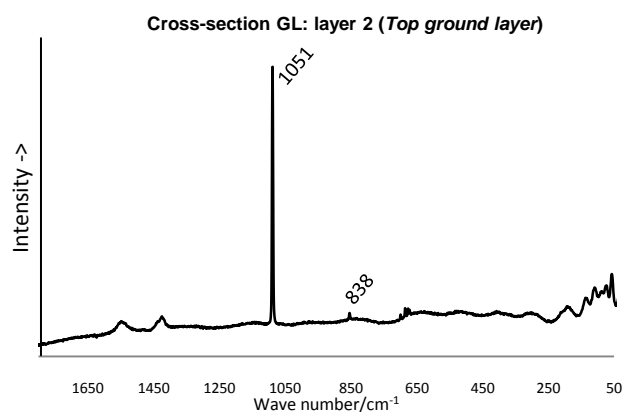


Fig. 41: μ -Raman Spectra of GL cross-section, layer 1 ($\lambda=632,81$ nm), showing the strongest characteristic lead white (cerussite) peak at 1051 cm^{-1} (21).

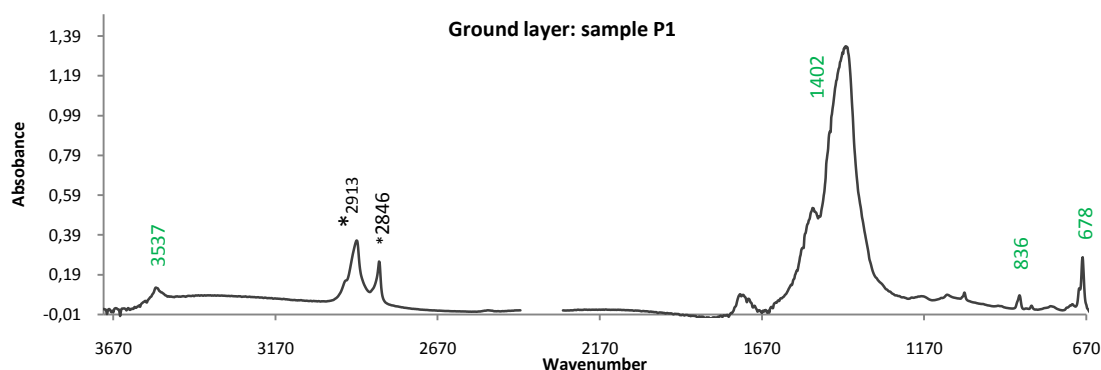


Fig. 42: IV Spectrum of Imprimitura (Sample P1). The Basic Lead Carbonate ($2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$) characteristic peaks are marked green (22). The peaks related to the linseed oil IR absorbance (27) are marked with black asterisk.

μ -XRF analyses				
Sample Identification		Color	Area	Elements Detected
Az1-Az6		dark Blue	Sky	Ca; Cr; Fe; Co; Zn ; Pb
B1-B7		white	Fist	Cr, Fe; Zn ; Pb
Cb1-Cb3		Black	Hair	Ca; Cr; Fe; Co; Zn ; Pb
Cal1-Cal6		Deep Blue/Black	Pants	Ca; Cr; Fe; Co; Zn ; Pb
T1-T3		Carnation	Front head/Carnation	Ca; Cr; Mn; Fe; Zn ; Pb
C1-C5		light brown	Fem. Fig. hair	Ca; Cr; Mn; Fe; Zn ; Pb
C6-C17		Brown	Figures left side	Ca; Cr; Mn; Fe; Zn ; Pb
Cin1-Cin3		Grey	Sky	Ca; Cr; Fe; Co; Zn ; Pb
R1-R3		Pink	Fist	Ca; Fe; Zn ; Pb
CC1-CC3		Light Brown	Jacket	Ca;Cr; Mn; Fe; Zn ; Pb
Prep1-Prep3		White	Ground Layer	Ca; Zn ; Pb
R1-R3		pink	Flesh tones	Ca; Fe; Zn ; Pb
V1-V3		Light Green	Left central side	Ca; Cr; Fe; Co; Zn ; Pb
V4-V9		Dark Green	Ground/Earth	Ca; Cr; Fe; Zn ; Pb
Ve1-Ve6		Red	Scarf	Ca; Cr; Fe; Co; Zn ; Se; Cd, Pb
Am1		Yellow	Troop's Flag	Ca; Cr; Fe; Zn ; Cd, Pb

Table 1: μ - XRF analyses results to *Sinfonia Heroica* painting

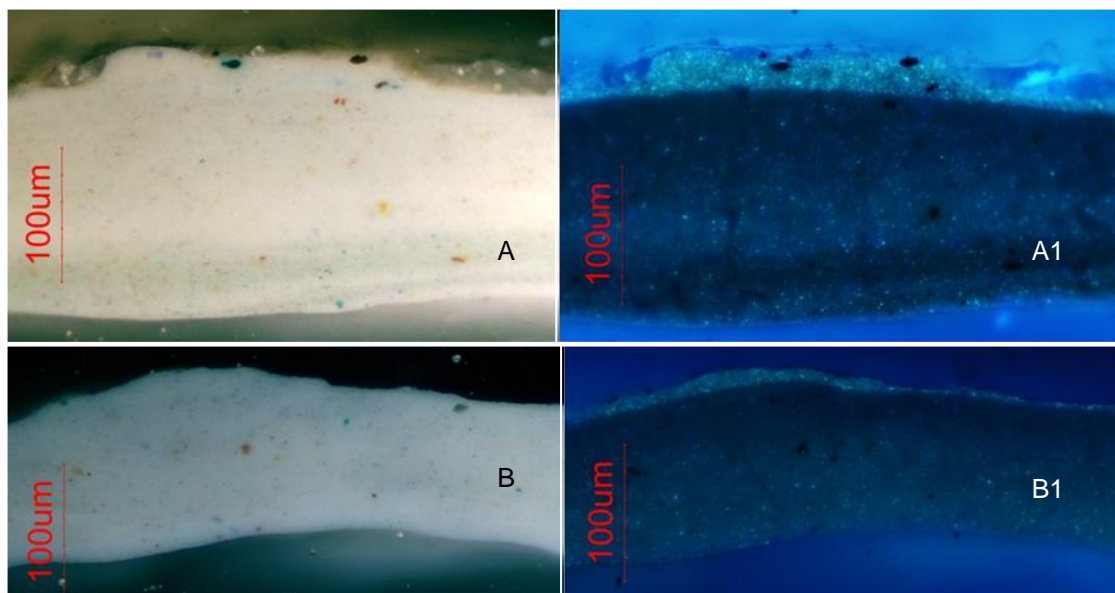


Fig. 43: A: Cross-section A 1.1 100x OM, visible reflected light; A1: UV light B: Cross-section A 1.2 100x OM, Visible, dark field polarized light; B1: UV light

Label A: CEMUP 15kV A2.1 Z1

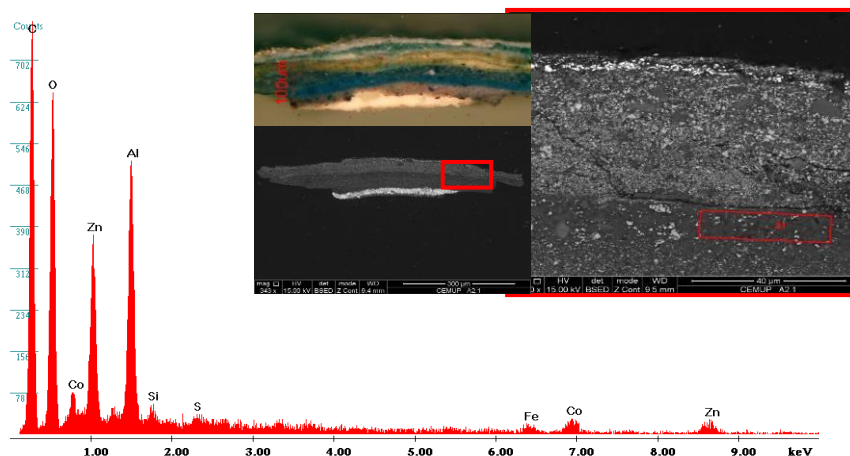


Fig. 44: SEM-EDX analysis on layer 6, from cross section IIA2, blue colour identifying the use of pigment cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$).

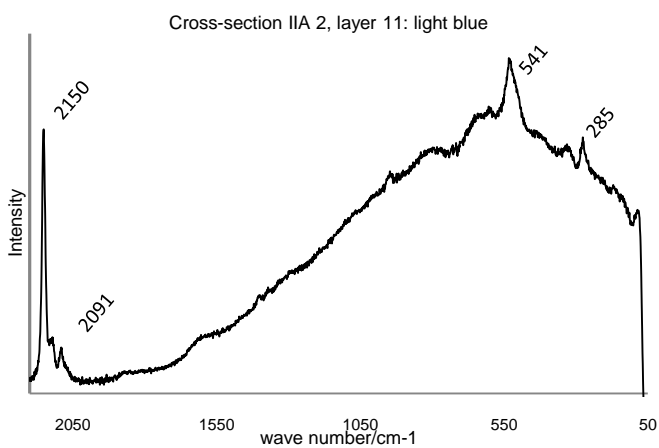


Fig. 45: μ -Raman spectra for layer 11, cross-section A2, showing the characteristic Prussian blue peaks (21).

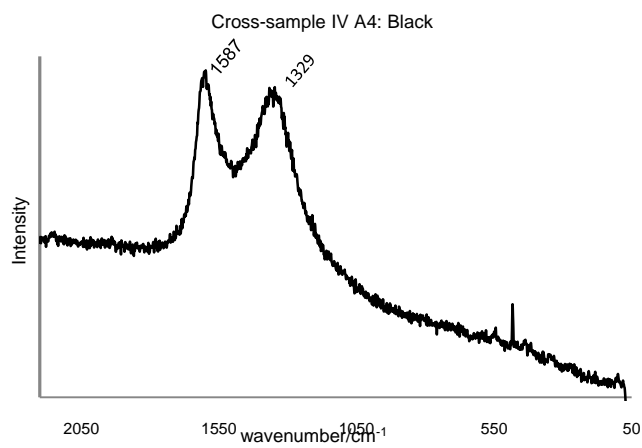


Fig. 46: μ -Raman spectra on cross-section A4, showing the characteristic Carbon black peaks (21).

APPENDIX XIV: PAINT TUBE ANALYSES

	Paint tube ID	Brand	μ-XRF analysis
●	Nº1 Ivory Black	Winsor&Newton	Ca ; Mn; Fe ; P
●	Nº2 Yellow Ochre	Winsor&Newton	Fe
●	Nº3 Venetian red	Winsor&Newton	Fe ; Ca
●	Nº4 Ultramarine Deep	Winsor&Newton	Ca; Fe
●	Nº5 Naples Yellow	Rembrandt	Zn
●	Nº6 Cobalt Blue light	Rembrandt	Ca; Fe; Co; Zn ; Ba
●	Nº7 Cadmium Yellow lemon	Rembrandt	Cd; Zn
●	Nº8 Prussian Blue	Rembrandt	K; Ca; Fe ; Zn
●	Nº9 Permanent light green	Rembrandt	Cr , Fe; Co; Zn ; Ba ; Pb
●	Nº10 Burnt sienna	Rembrandt	Ca; Fe
●	Nº11 Rouge de Cadmium	Lefranc	Fe; Zn ; Pb; Se ; Cd

Table 2: List of Dordio's paint tubes and their μ-XRF analysis results. In bold are marked the elements with the greatest X-ray Fluorescence intensity. The zinc element present in the tubes is marked in blue Winsor & Newton Paint Tubes IV Spectra

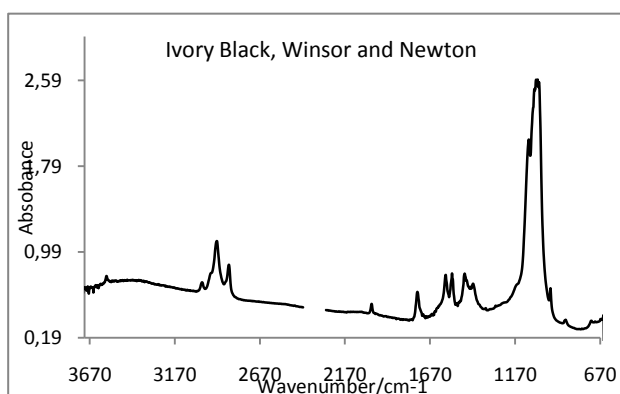


Fig. 47: μ -FTIR spectrum of Dordio Gomes W&N Ivory Black paint tube.

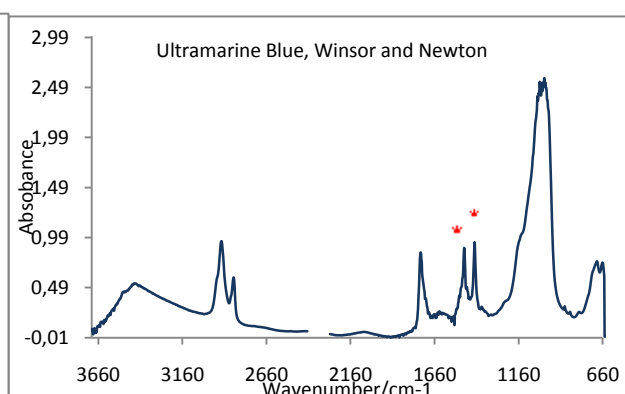


Fig. 48: μ -FTIR spectrum of Dordio Gomes W&N Ultramarine Blue paint tube. Magnesium sulphate filler is marked with red.

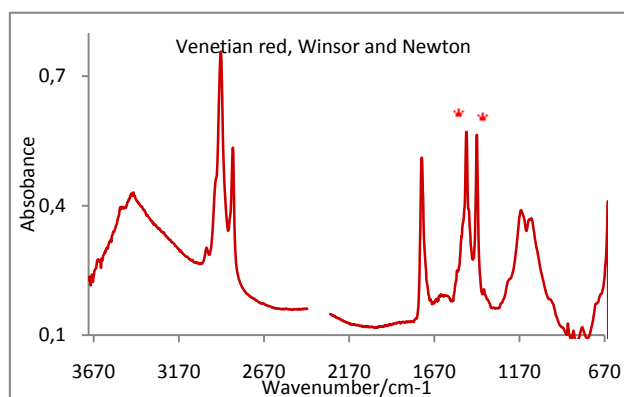


Fig. 49: μ -FTIR spectrum of Dordio Gomes W&N Venetian red paint tube. Magnesium sulphate filler is marked with red.

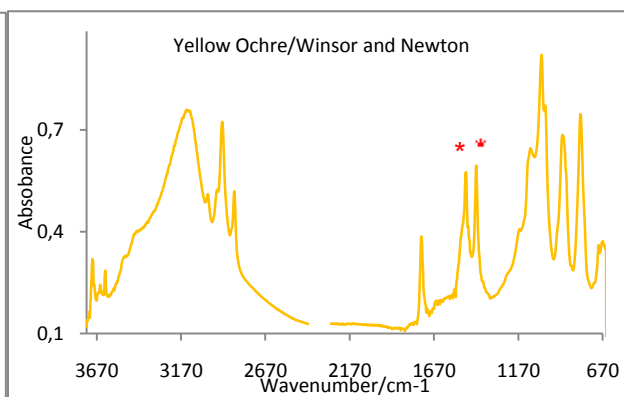


Fig. 50: μ -FTIR spectrum of Dordio Gomes W&N Yellow Ochre paint tube. Magnesium sulphate filler is marked with red.

APPENDIX XV: REMBRANDT AND LEFRANC PAINT TUBES μ -FTIR SPECTRUM

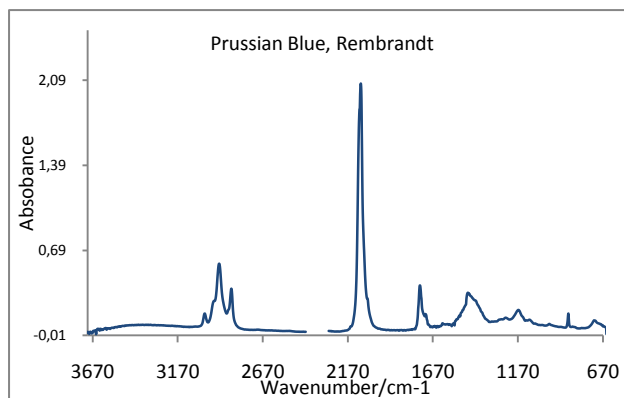


Fig. 51: μ -FTIR Spectrum for Rembrandt Paint tube Prussian Blue.

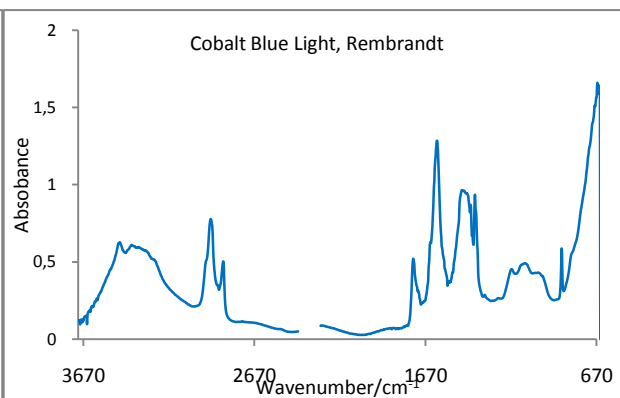


Fig. 52: μ -FTIR Spectrum for Rembrandt Paint tube Cobalt blue light.

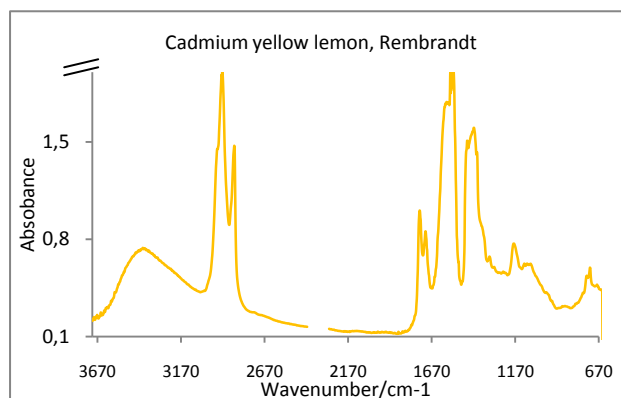


Fig. 53: μ -FTIR Spectrum for Rembrandt Paint tube Cadmium yellow Lemon.

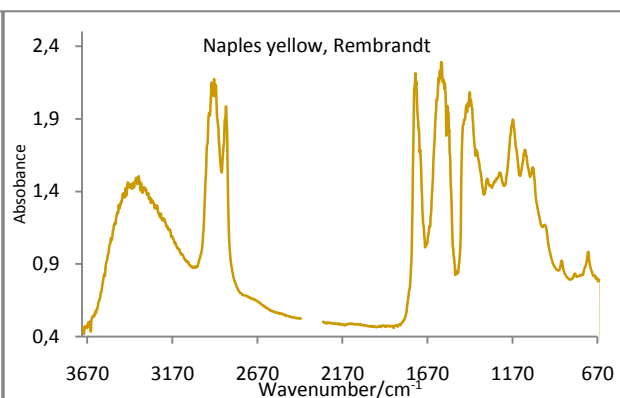


Fig. 54: μ -FTIR Spectrum for Rembrandt Paint tube Naples yellow.

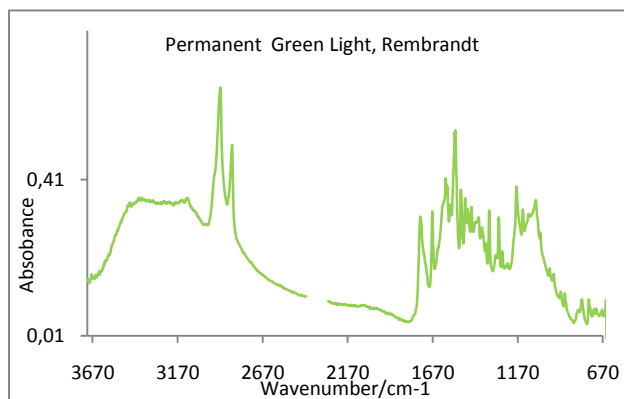


Fig. 55: μ -FTIR Spectrum for Rembrandt Paint tube Permanent Green Light.

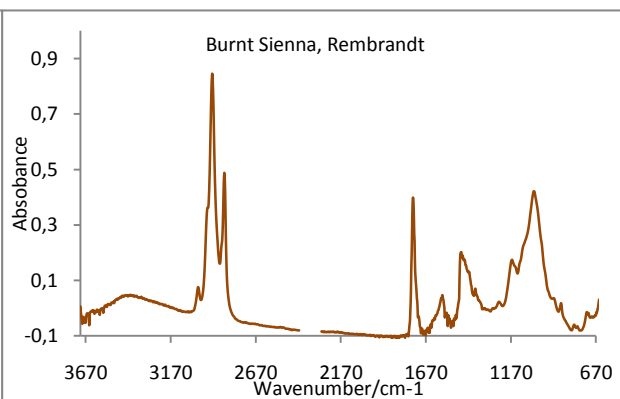


Fig. 56: μ -FTIR Spectrum for Rembrandt Paint tube Burnt Sienna.

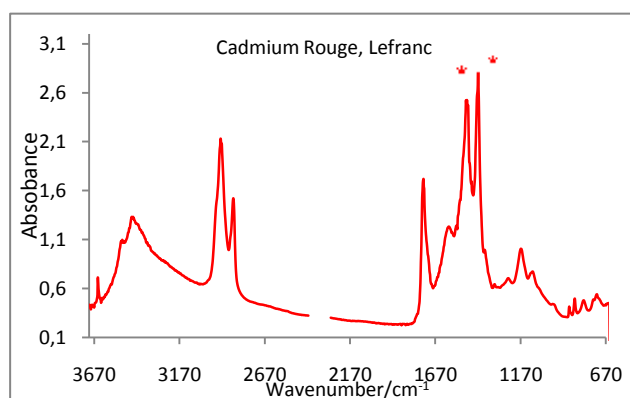


Fig. 57: μ -FTIR Spectrum for Lefranc Paint tube Cadmium Rouge. Magnesium sulphate filler is marked with red.

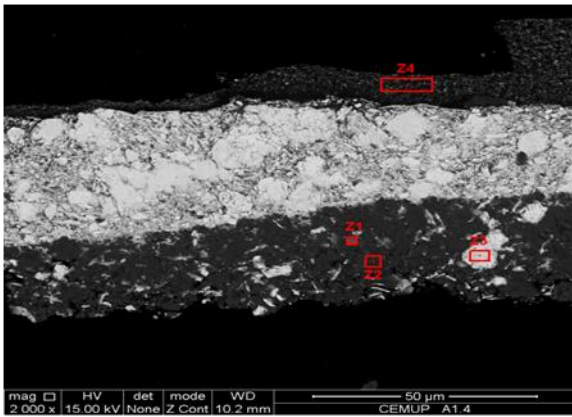


Fig. 58: Backscattered image of cross-section I A1.4. The squares show the SEM-EDX analysis areas.

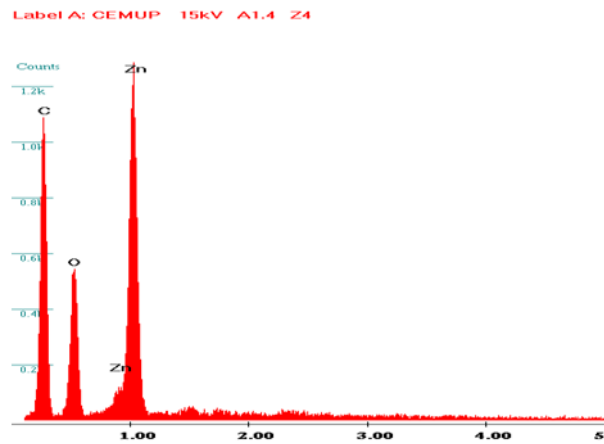


Fig. 59: SEM-EDX Spectrum on I A1.4 (Z4) top layer analysis.

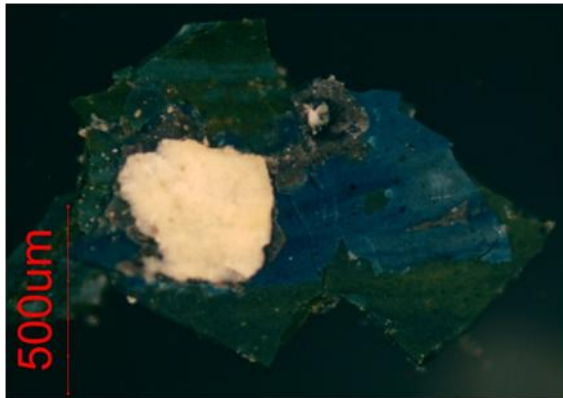


Fig. 60: MO image of sample A20 showing interlaminar cleavage between paint layers. 500x mag., visible reflected polarized light.

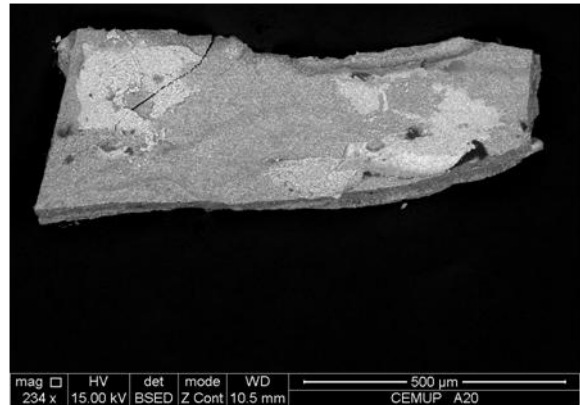


Fig. 61: Backscattered image of sample A20.

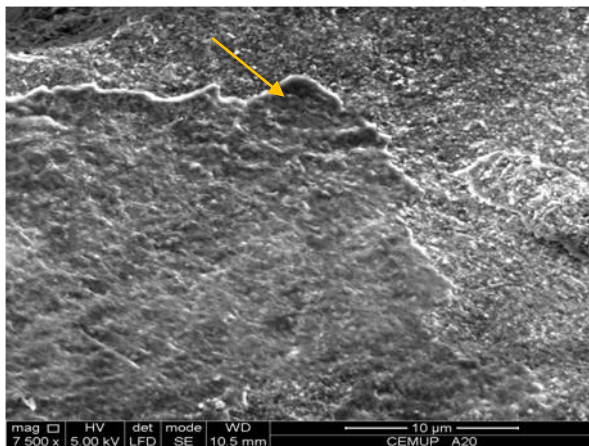


Fig. 62: Secondary electron detail image of sample A20. Can be seen a translucent layer on top of the painting layer that can be due to the migration of the binder.

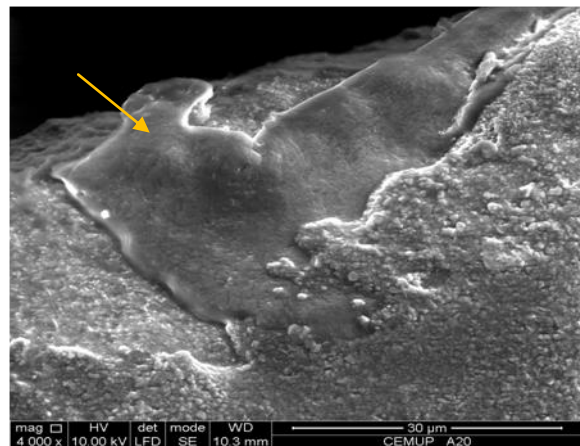


Fig. 63: Secondary electron image detail of cross-section A20, showing a translucent/viscous layer standing in between the two painting layers.



Fig. 64: Surface cleaning of the painting with soft cotton swabs moistened with distilled water and Surfynol 61®.

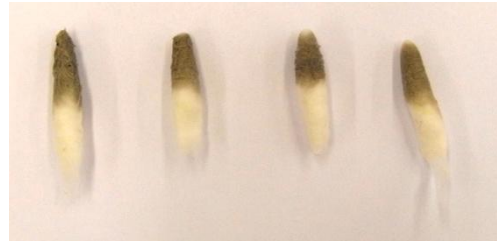


Fig. 65: Colour of the cotton swabs after surface cleaning, indicating the amount of dirt on the painting's surface.

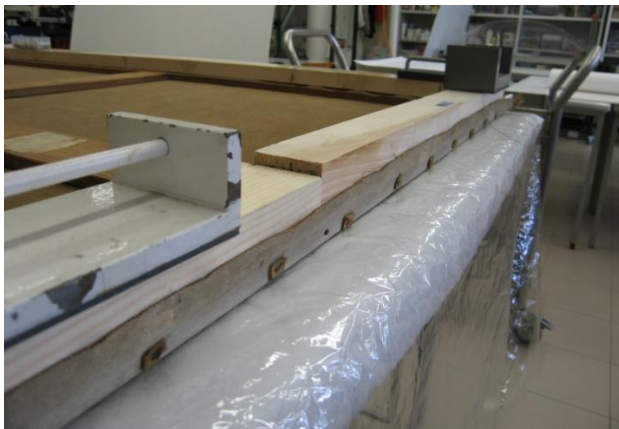
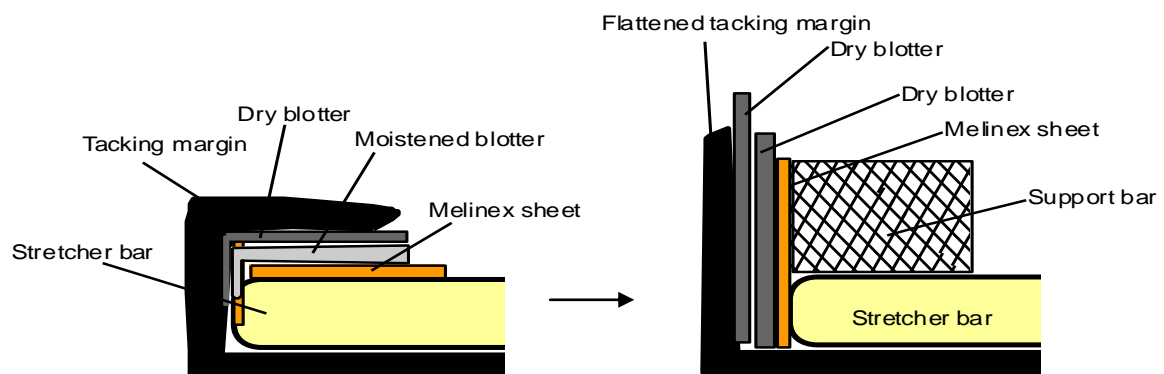


Fig. 66: Flattening of the back of the tacking margins. The weights were used to hold the margins straight.



Fig. 67: Picture of the painting facing down without stretcher bars and with the flattened back of the tacking margins.



Flattening of the Tacking margins

Fig. 68: Cross-section scheme of method used to flatten the back of the tacking margins.



Fig. 69: Placement of the polyester thin sheet on top of reverse.

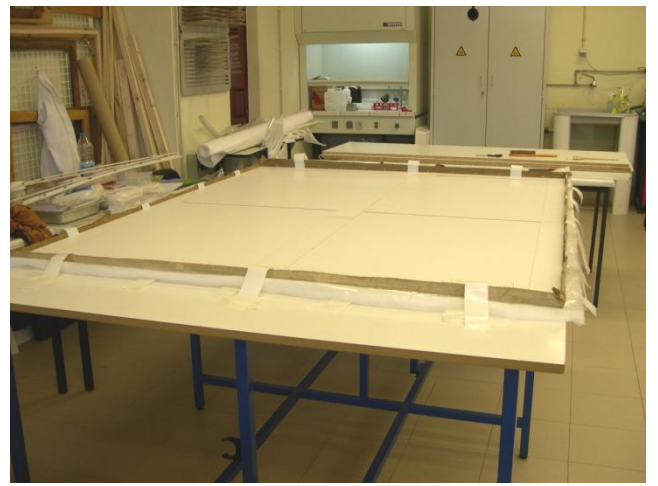


Fig. 70: white plain board card placed on top of polyester sheet.



Fig. 71: Placement the stretcher bar on top of the white plain board cards.



Fig. 72: Kapa-line built up squares to place between the stretcher bars.



Fig. 73: Painting "sandwich". Method used to turn the painting without it being attached to the stretcher.



Fig. 74: Construction of the moisture chamber.



Fig. 75: Moisture chamber.



Fig. 76: View from inside the moisture chamber. Below: the painting; in the center: Termohygrometer detector; upper: metal screen with moistened blotting papers on top.



Fig. 77: View of *Sinfonia Heróica* inside the moisture chamber, used for the flattening treatment.



Fig. 78: Placing the flat wood boards on top of the painting.



Fig. 79: Weights placed on top of the flat wood boards, for pressure.



Fig. 80: view of the Painting with raking light after the flattening treatment.



Fig. 81: view of the Painting with raking light after the flattening treatment.



Fig. 82: Holding the painting for the application of steel tacks.

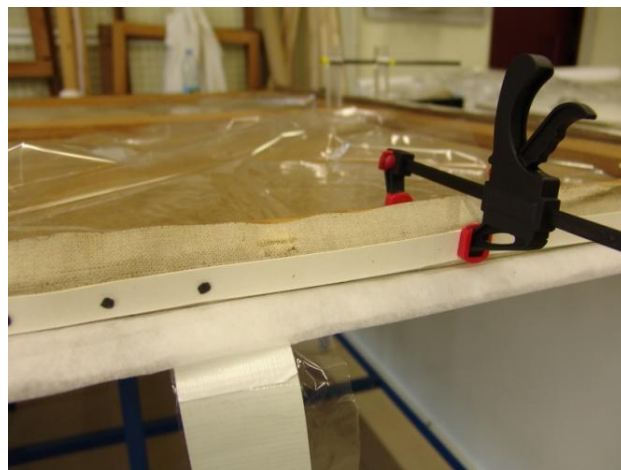


Fig. 83: Application of steel tacks.

For the conservation treatment, a study of infill materials and application methods was carried out. Nine different infill materials were prepared and applied on hemp canvas (fig.84, below) . Each infill method was evaluated for :

- 1-Application
- 2- Trespass
- 3- Drying time
- 4- Colour after drying
- 5- Texture
- 6- Drying Cracks (cohesion)
- 7- Cracks when applying a perpendicular force from the back
- 8- Elasticity
- 9- Reversability
- 10- Sensitivity to organic solvents
- 11-Multi-layer application

The results are shown in table 3 (next page).

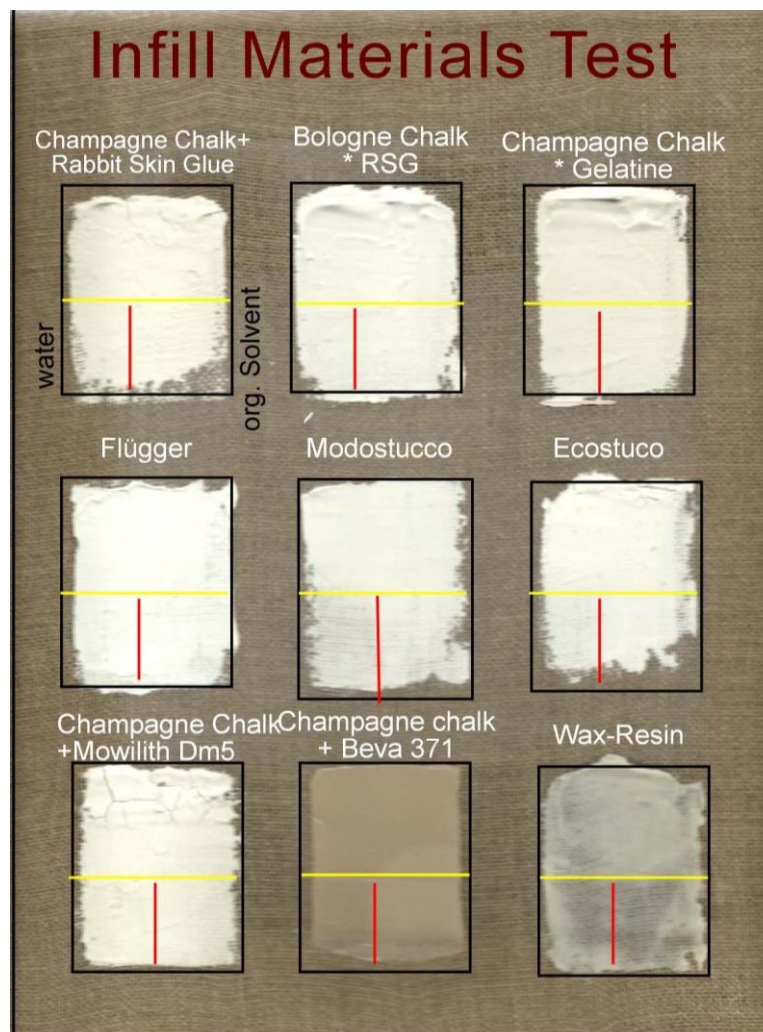


Fig.84: Infill Materials Test. Linen canvas with nine different infill materials tests.

	Champagne Chalk (CC)+ Rabbit skin glue (RSG)(5%)	Bologne Chalk+RKG (5%)	CC+gelatine (10%)	Flügger®	Modostuco®	Ecostucco®	CC + Mowilith DM5 (25%)	CC+Beva 371 (1:2)	Wax/Resine Recipe
Materials	Chalk: Kremer Pigments (ref:58000); RSG: Kremer Pigments (Ref:63028)	Chalk: Kremer Pigments (ref:58100); RSG: Kremer Pigments (Ref:63028)	Chalk: Kremer Pigments (ref:58000); Gelatin: Kremer Pigments (Ref:63045)	Flügger®		Ecostucco: Borma Wachs (Promoble)	Chalk: Kremer Pigments (ref:58000); Mowilith DM5: Productos de Conservación	Chalk: Kremer Pigments (ref:58000); Kremer Pigments; Beva 371: CTS-Productos de conservacion	Bees Wax; Dammar Resin; Elemi Resin
Preparation mode	The chalk was added to the RSG glue sol. until reaching a mayonnaise consistency	The chalk was added to the RSG glue sol. until reaching a mayonnaise consistency	The chalk was added to the gelatin glue sol. until reaching a mayonnaise consistency	Ready to use	Ready to use	Ready to use	The chalk was added to the mowilith glue sol. until reaching a mayonnaise consistency	(Petria Noble's recipe)	7 parts Bees Wax; 2 parts Dammar Resin; 1 part Elemi Resin (Ready to use)
Application	Spatula. Good Control even surface	Spatula. Good Control even surface	Spatula. Good Control even surface. Very smooth	Spatula. Good Control. Very even surface	Spatula. Good Control. Very even surface.	Spatula. Good Control. Very even surface	spatula	Hot spatula. High temperatures (70° depending on the thickness). Acquires all textures	Melted on hot plate; application with spatula. Hot temperature. Can only be applied when melted.
Trespass	no	no		yes	yes, very		no	no	yes
Drying time	2.30-3h	2.30-3h	2.30-3h	2h	2h	2h	3h	5 min	immediately
Colour after dry	grayish	white	grayish	white	white	white	beige	brown	crème
Texture	smooth	smooth	very smooth	smooth	smooth	smooth	texturized	very smooth	very smooth
drying cracks	Yes, when thick	no	no	yes when thick	no	no	Yes, extensive. In all area.	no	no
cracks when applying a perpendicular force on the back	yes, with no preferential direction	Only in the thick layer	Only in the thick layer. In the thin one shows little cracks that get back to normal	Does not show cracks in the thin layer	Does not show cracks in the thin layer	Does not show cracks in the thin layer	yes, with detachment	no	no
Elastic behavior	stays the same	stays the same	stays the same	stays the same	stays the same	stays the same	stays the same	rigid	stays the same
Reversibility	water	water	water	When wet, with water.	water	water	water	white spirit	white spirit
sensitivity to organic Solvents	no	no	no	white spirit	no	no	no	yes	yes
Multiple applications	yes	yes	yes	yes	yes, very	yes	yes	yes	Yes

Table 3: Results of infill materials test

